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IMPERFECTIONS IN MATTER

by G. W. RATHENAU *).

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*An important stage is reached in a field of research when we are able to distinguish between phenomena inherent in an idealised system and others which are due to disturbances or imperfections in this system. The concept of an "ideal" or "perfect" state is prompted by a desire for simplicity which, it would appear, is not shared by nature. Evidently the dynamic of the human spirit is not based on the same "minimum principles" which govern the processes of nature. Prof. G. W. Rathenau, in his inaugural lecture delivered on 16th March 1953 at Amsterdam, elaborates on this theme and describes its application to the special field of the structure of solids. The main points of this inaugural address, supplemented with illustrations and a bibliography, are reproduced here with the kind consent and co-operation of Prof. Rathenau **).*

Introduction

Matter in the solid state plays an exceptionnally important part in our lives. The tools which man has evolved are witness to the unique qualities of solid matter, and the evolutionary ages of man bear the names of materials. It is an open question what name will be given by posterity to the present age, for which the press has already introduced the unfortunate title of atomic age. One thing is certain, however, that the technical and social significance of the discovery of nuclear energy largely derive from the fact that new fuels are now available for driving our machines.

As far as we ourselves are concerned, the human frame has all the characteristics of solid substance, even though opinions of the importance of this vary between the extremes of Epictetus, who regards the human being as a soul bearing the burden of a body, and of Nietzsche's view "Leib bin ich ganz und gar, und nichts ausserdem; und Seele ist nur ein Wort für ein Etwas am Leibe". (I am wholly body and nothing else; the soul is only another name for a part of the body).

Bravais, a hundred years ago, was the first to regard crystalline solids as consisting of atomic particles arranged at uniform intervals, to form periodic lattices in space. Not until 1912 did the work of von Laue and co-workers brilliantly confirm the main parts of this idea.

The last 40 years have shown that the application of theory, and particularly the quantum theory, to the model of the space lattice paves the way to an explanation of many of the properties of solids.

On the other hand, owing to mathematical difficulties and the lack of precise physical representations, the model of the space lattice has so far not been developed to the point where important properties such as supraconductivity and the magnetic saturation of metals can be satisfactorily explained.

It may, at first sight, seem surprising that so much of the theoretical and experimental work on the solid state in recent years has been concerned with the *imperfections* in the space lattice, while the model of the *perfect* space lattice is still in need of further development. The explanation of this apparently illogical development must be sought in the fact that small divergences in the periodicity have a pronounced effect on the characteristics of the substance. The situation is very analogous to that of a cobbled road with a number of stones missing after every thousand. From an aircraft, the road would appear to be perfect, but a motorist would consider it a very poor approximation to a road: from the point of view of driving its usefulness depends on the presence or absence of the defects.

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The terms "periodicity deviation" and "lattice imperfection" would seem to imply an unfavourable appraisal not only of the matter itself, but also of this whole field of research. Caution is necessary in any such qualitative appraisal, however. In the history of scientific research it is often the case that divergences found experimentally from an idealised model have proved to be pointers to theoretically and technologically important developments. Furthermore, when imperfections appear to be *inevitable* and should therefore be referred to as the "rule" rather than as imperfections or defects, their investigation is clearly justified.

In fact, particularly in recent years, it has been shown that lattice imperfections are indeed inevitable.

The rôle of entropy in the occurrence of lattice imperfections

It is a well-known fact that the production of lattice defects in a crystal system involves an increase of internal energy. At the same time, it is possible to indicate two general causes of the inevitability of such defects. The first of these is related to a very universal premise which states that with rising temperature the macroscopic state of an atomic system is determined less and less by the requirement of lowest internal energy and more by the requirement of a large number of ways of obtaining this state. Stated in more general terms, this means that at elevated temperatures, nature does not tend towards order, but towards disorder. Hence well-ordered crystals undergo a change at the higher temperatures to the liquid or gaseous state, in which the atoms are less well arranged. The lattice imperfections, whose equilibrium concentration increases with temperature, tend to make the solid state resemble the molten or gaseous phase. From the statistical point of view the state implied by the word "disorder" could, in fact, be termed "order", just as an untidy writing desk, viewed from a higher level may, in fact, be considered as being more ordered than one on which all the papers are concentrated in one heap.

Let us take the case of a crystal consisting of atoms of one kind only. Atoms of one kind may be regarded as indistinguishable from each other, so that the crystal can be constructed in only one way. If one atom of another kind be introduced, however, the conditions are very different. A given macroscopic condition, e.g. a crystal with a foreign atom somewhere within it, can be constructed in just as many ways as there are possible positions of the foreign atom in the crystal. The same will apply mutatis mutandis to atomic vacancies in a crystal, and for all other local departures from uniformity.

Many solids are formed at such high temperatures that the number of realisation possibilities — expressed in terms of the entropy — will significantly influence the concentration of imperfections. It is not improbable that, for special applications, advances in technique may lead to lower temperature methods of preparation of solids, which can now be formed only at elevated temperatures. Often, however, it is found that the limit of chemical purity indicated by entropy has not been reached by a long way. In three dimensions, the analogue of our example of the cobbled road, viz, one impurity at 1000 atomic intervals, may, in fact, be called a model of perfection.

Interaction between physical lattice defects and departures from stoichiometry.

In a study of this kind it is an over-simplification to regard divergences from exact chemical composition, i.e. departures from stoichiometry, as independent of physical departures from uniformity, such as vacancies in the lattice. Often the internal energy of a crystal can be reduced by introducing a chemical defect together with a physical imperfection. A well-known example of this is given by Bradley and co-workers [1]) in the ordered nickel-aluminium alloy NiAl with a surplus of aluminium. From the point of view of minimum energy it is more advantageous to leave two places *vacant* in the nickel sub-lattice than to squeeze a large aluminium atom into one of the places belonging to the small nickel atom. The same argument explains why in ionic lattices such as that of ferrous oxide FeO, a surplus of oxygen is in fact obtained by the formation of unoccupied places in the lattice of the iron.

This last example may be used to show that the introduction of extra oxygen may have further consequences in addition to the occurrence of physical defects in the form of unoccupied places in the ionic lattice. In fact, as far as energy is concerned, it is most advantageous to make the entire crystal electrically neutral. This can be done by the formation of trivalent iron ions as additional lattice faults. One kind of lattice defect is then responsible for a whole chain of defects. Future work will have to be awaited for an atomic scale-picture of the situation in ionic crystals containing more complex defects such as dislocations. The fact that the valency of the participating ions can be controlled by the introduction of suitable chemical additions in ionic lattices has been shown by Verwey and co-workers ²). In this way the electrical conductivity and diffusion rate in the solid state, i.e. the reactivity, can be controlled. The problems concerned are particularly important from a technical point of view. Among others, Wagner ³), Mott ⁴) and Shockley ⁵) have made contributions to their solution.

Mention has been made of a physical defect arising from a chemical imperfection; this is an extreme instance of interaction. More usually, physical and chemical lattice irregularities already present, attract or repel each other. Examples of this are found in the work arising from Snoek's research on interstitial solutions ⁶); small atoms occupy intermediate lattice positions in crystals built up from larger atoms. It appears that these small atoms migrate to those places where there is a physical lattice defect which offers them more space. When the crystal is elastically stretched, they arrange themselves more or less in the direction of elongation (*fig. 1*). If permanent, additional lattice defects are produced as a result of plastic deformation, the interstitially dissolved atoms are captured within them, as shown by Dijkstra ⁷). The material can accordingly be purified locally by heaping up the impurities at some other point.

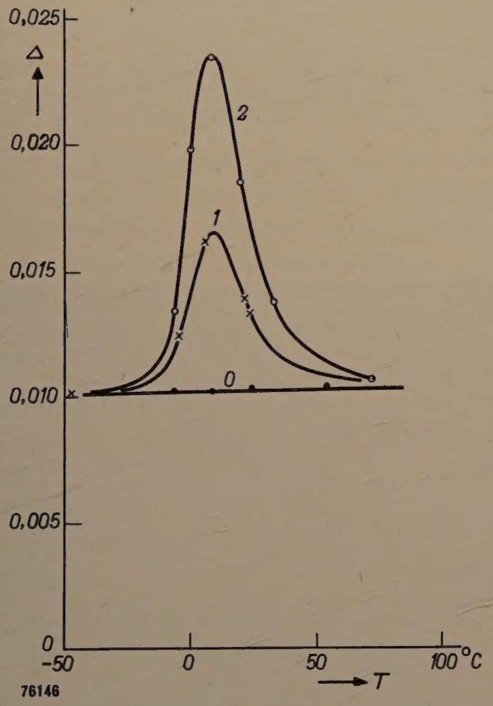


Fig. 1. Damping Δ of torsional vibrations in iron as a function of the temperature T. The damping is caused by the migration of dissolved nitrogen atoms to sites offering them the most space. These atoms thus arrange themselves more or less along the direction of tensile stresses, subject to a certain relaxation time. If the oscillation period is equal to 2π times this relaxation time, a relatively large amount of the vibrational energy is absorbed and dissipated as heat. A damping peak therefore results.
0: wire of pure iron
1: iron wire with dissolved nitrogen
2: as *1*, but with greater quantity of nitrogen
(From J. L. Snoek, Physica **8**, 711-733, 1941).

It is clear that research in this newly opened field, as undertaken for example by Zener ⁸), Cottrell ⁹) and Fast ¹⁰), is only at a beginning. It is difficult to believe that the accommodation of dissolved atoms is determined only by the amount of space available for them. For that matter it is not at all certain in what state of ionization the interstitially dissolved atoms occur and whether this ionization does not in turn depend on the surrounding structure. It is possible that sensitive methods of measurement may yield further information on these questions.

Acceleration of structural changes by lattice imperfections

As a first reason for the inevitability of lattice irregularities, the entropy gain which they occasion has already been mentioned. When the crystal is at an elevated temperature, the internal energy will rise if irregularities occur, but the free energy — which decides what will really happen — will decrease.

The second reason for the occurrence of lattice defects is that, in general, nature by no means always selects a path for structural changes that leads *direct* to the greatest decrease in free energy of the system. Nature takes the *quickest* route compatible with the requirement of a drop in free energy in the whole system. In systems involving structural changes in the solid state, this speed is often achieved at the expense of the perfection of the lattice. One may be permitted to say that nature behaves as a mass producer, preferring a quick sale at low profit.

Crystal growth from solutions; nucleation as a rate-limiting factor

Frank and co-workers ¹¹) have concerned themselves with the growth of crystals especially from supersaturated solutions. Their investigations are of great importance as the treatment is straightforward and the confirmatory experiments unambiguous. Consider the case of a perfectly faced crystal in a moderately supersaturated solution.

The first atoms, which by adsorption could form an atomic layer on the perfect crystal face, parallel to it, are very liable to be re-dissolved, for the evaporation pressure of the nucleus of the new layer is very high as long as its volume is small compared with its surface. However, once a nucleus of a certain critical size has been accidentally formed — an improbable event in itself — it can grow rapidly and thus produce another perfect face on which, after an indefinite time, a fresh nucleus of critical size may be adsorbed.

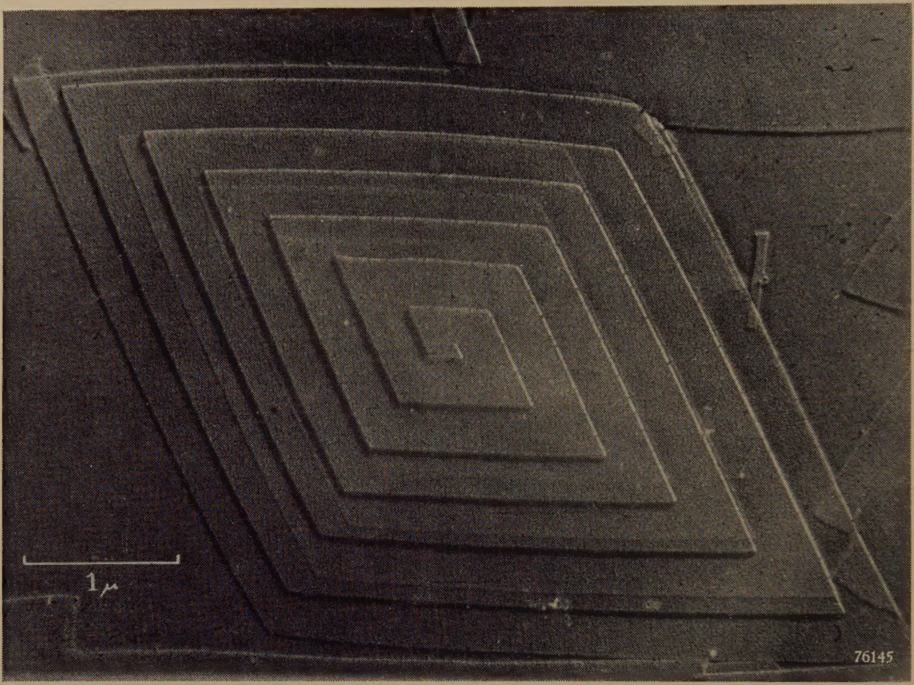


Fig. 2*a*) Growth of a single crystal of n-hectane in the direction of the axis of a screw dislocation. Electron-microscope photograph; specimen shadowed with palladium. (I. M. Dawson, Proc. Roy, Soc. A **214**, 72-79, 1952, No. 1116).

In the example given, the repeated nucleation is the process that determines the speed of the reaction. It can be avoided by building the crystal on the principle of a single continuous surface, much as the surface of a screw thread or that of a spiral staircase can be regarded as constituting a single surface. If a crystal exhibits a *screw dislocation* of this kind, it can grow further in the direction of the axis of the spiral without requiring repeated nucleation from which fresh faces can grow (*fig. 2a* and *b*).

For crystal growth, therefore, what is needed is a dislocation such that the Burgers vector characterising the imperfection (so called after J. M. Burgers who has done much pioneering work on dislocations) includes a component in the direction of the normal to the plane of the lattice. In the absence of a dislocation of this kind, growth is practically at a standstill.

In the case in point, imperfections in periodicity are thus essential to growth. Whoever compares the experimentally found growth spirals — of which fresh examples are given almost daily —

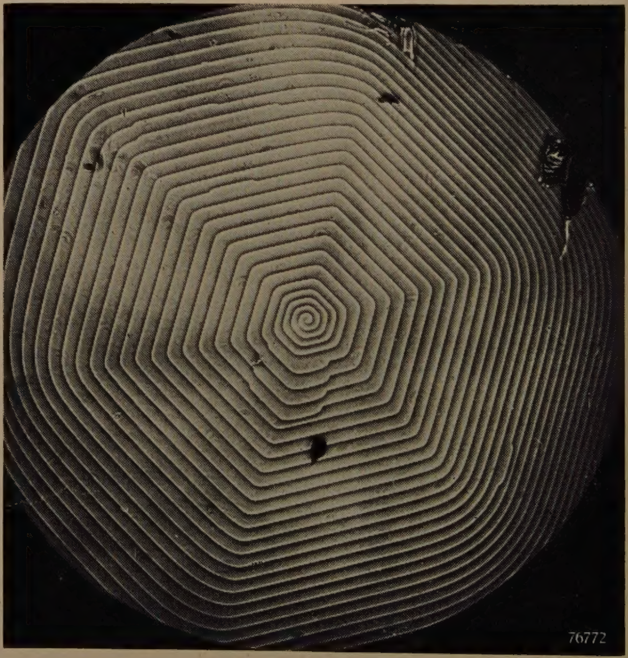


Fig. 2*b*). Growth spiral on a carborundum crystal. (A. K. Verma, Nature **168**, 430, 1951).

with the calculated forms cannot doubt the essential correctness of this statement. If the distance between the successive turns of the spiral along the axis is large, possibly owing to the presence of a large and rather complex unit cell in the structure, it may be expected, moreover, that that space round the axis of the spiral, which is under the most elastic strain, will be "channelled" and not filled with atoms [12]). Until now, examples of this phenomenon have been obtained experimentally only in inorganic substances. It would be surprising, however, if no use were made in living matter of this opportunity for the formation of very fine capillaries.

It might well be asked: to what should we attribute the screw dislocation that promotes the growth of a crystal? It is probable that this physical imperfection will, again, often arise as a result of variations in the chemical composition — corroborating the proverb that accidents never happen singly.

I should not wish to create the impression that the theory propounded by Frank is capable of explaining more than a small part of the phenomena of crystal growth from the liquid phase. Suffice it for me to say that it is at the moment not quite clear how the terms "supersaturation of a solution" and "perfect interfaces" should be interpreted when applied to crystal growth from a melt. It is not improbable that the imperfection in crystals formed from the melt (as revealed by X-ray diffraction) is to a certain extent also unavoidable.

Segregation; diffusion as a rate-limiting factor

In the growth of crystals from supersaturated solutions, of which we have just spoken, the nucleation is the rate-limiting factor. In order to grow *without* repeated nucleation — that is to say, rapidly — the crystal awaits the occurrence of lattice imperfections. In other transformations of solids there are rate-limiting factors of a different kind. A typical example is found in iron-carbon alloys, which form homogeneous crystals at elevated temperatures. At relatively low temperatures these crystals must, in order to attain equilibrium, separate to form two quite different kinds of crystal which also both differ from the original in structure and carbon concentration. Here, it is the diffusion of the carbon that determines the rate of transformation. In fact, the carbon appears almost only in one of the final phases.

In order to increase the speed of the reaction, nature reduces the path along which diffusion has to take place, viz. by forming the two new crystal types as lamellae in alternating layers (*fig. 3*). At the *boundaries* between two such lamellae, imperfections occur, simply owing to the fact that the two lattices do not mate. During the transformation, therefore, a part of the available free energy is transferred to energy at the boundary planes.

According to an estimate of Zener [13]), who has made a theoretical investigation of such transformations, about half the energy released during the transformation should be retained as boundary energy, in order to give the highest reaction rate. The lower the temperature at which the transformation takes place, the lower the rate of diffusion, but the greater the amount of free energy available for the formation of new boundary planes. As a result, a finer spacing of the lamellae occurs, a fact which has been known for some time from experiment. A theoretical minimum for the lamellae spacing, as indicated by the energy at the boundary plane and the heat of transformation would lie in the region of 200 Å.

Even though the principal factors are known, the transformations that take place in steel have yet to be studied very much more closely. It is not yet known, for example, whether and when a relationship exists between the orientation of the lattices of the two lamellate types of crystal.

Segregation; various rate-limiting factors

Whereas in the first-mentioned class of structural changes, nucleation is the rate-limiting factor, and in the second example the diffusion, it is to be expected that frequently one and the same substance will encounter different rate-limiting factors in different temperature ranges. Nature employs various devices to evade these.

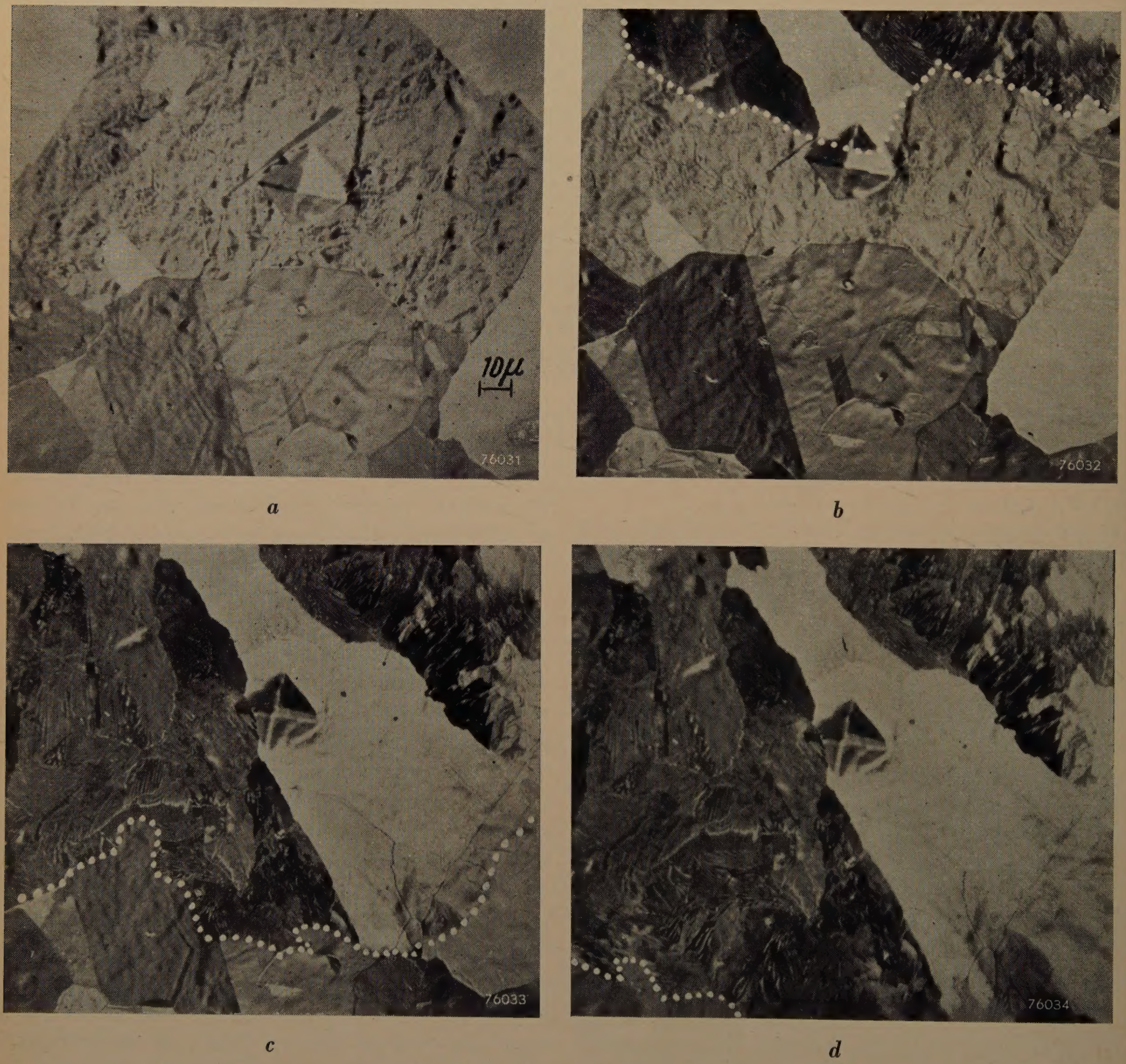
Crystals supersaturated with a given element, as investigated by Guinier [14]) and Köster [15]), furnish eloquent examples of this. Below a certain temperature the solid solution is no longer stable. Just below this transition temperature there is so little free energy available that the surface energy essential for the formation of a germ crystal cannot be produced. In this temperature region, germ crystals occur as parasites on any lattice imperfections that may be present, which reduce the surface energy required and thus promote an acceleration of the process. In this way the lattice imperfections become permanently fixed. At temperatures well below the transition temperature, more free energy is available to reduce the supersaturation to zero, but diffusion now takes much longer, and precipitation from the supersaturated solution therefore occurs everywhere in the lattice of the matrix. This involves the consumption of considerable energy for the formation of lattice irregularities. The precise physical picture of this process can only be conjectured; one experimental indication is that in this low temperature region the separation appears to be reversible. An increase in temperature results in solution.

Finally, at very low temperatures, the rate of diffusion is so small that concentration differences even over very small distances require a great deal of time to develop. Transformation then takes place as a sudden reaction, the whole structure of the lattice undergoing a change whilst retaining the original composition; this structure is not stable, but it is more stable than the original one in the supersaturated state. The dimensional and angular changes accompanying this instantaneous reaction lead to an upheaval in the lattice and a large accumulation of energy in the resulting lattice defects.

It is possibly relevant to note that the physical picture of the relationships between the orientation of the vanishing lattice and of the lattice in process of formation is still very incomplete.

Recrystallization

During the growth of crystals in the homogeneous



a *b*

c *d*

Fig. 3. Formation of pearlite during cooling of an iron-carbon solution from high temperatures. The pearlite forms in colonies of small lamellae. The progress of the boundary of the pearlite formation is shown by the dotted lines in *b* to *d*. Photograph taken with an emission electron microscope constructed at Eindhoven (See G. W. Rathenau and G. Baas, Physica **17**, 117-128, 1951). Magnification 500 ×.

solid phase it commonly occurs that energy for the formation of lattice imperfections is partly diverted to ensure that the disappearing lattice will vanish as quickly as possible. We know that when metals are plastically deformed, the disturbances in the lattice due to this will, when the temperature is raised, line up in continuous planes, thus forming boundaries between undistorted, submicroscopic zones, with very slight mutual disorientation among the lattices. The phenomena of recovery and recrystallization, on which W.G. Burgers and co-workers [16]) have done such important work, are apparently based on nothing else than the development of these zones into larger areas.

For many years C. S. Smith [17]) has stressed the fact that the motive force in the growth of crystals in the homogeneous solid phase is the interfacial tension at the boundary planes, just as in the growth in a system of soap bubbles. From this it follows that small crystals are no match for larger ones, but that crystals of which the lattice shows only slight disorientation have little tendency to absorb each other. This is because the surface tension is very small when the disorientation angle approaches zero (*fig. 4*), a fact which is quite plausible and which is quantitatively demonstrated by the calculations of Read and Shockley [18]) and others, and by the experiments of Chalmers, Dunn and others. The fact that crystals with roughly similar orientation are not in a position to react with each other quickly, means that they can grow independently of each other, and that lattice disturbances become permanent at the common boundaries (even though they may not be very numerous per square cm).

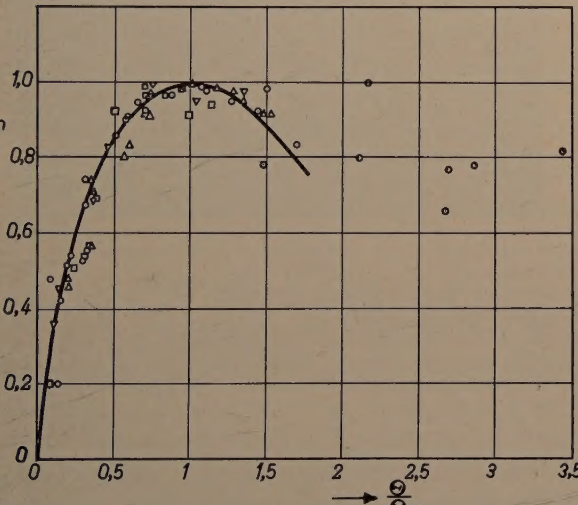


Fig. 4. Interfacial tension E (energy per unit area) of two crystals disoriented by an angle Θ with respect to each other. The various measurement points refer to three different metals. (W. Shockley, L'Etat solide, Inst. Internat. de Phys. Solvay, Brussels 1951, p. 447.) If Θ_m be the angle at which E is at a maximum ($=E_m$), E/E_m appears to be (to a fair approximation) the same function of Θ/Θ_m, independent of the metal.

Order-disorder transitions

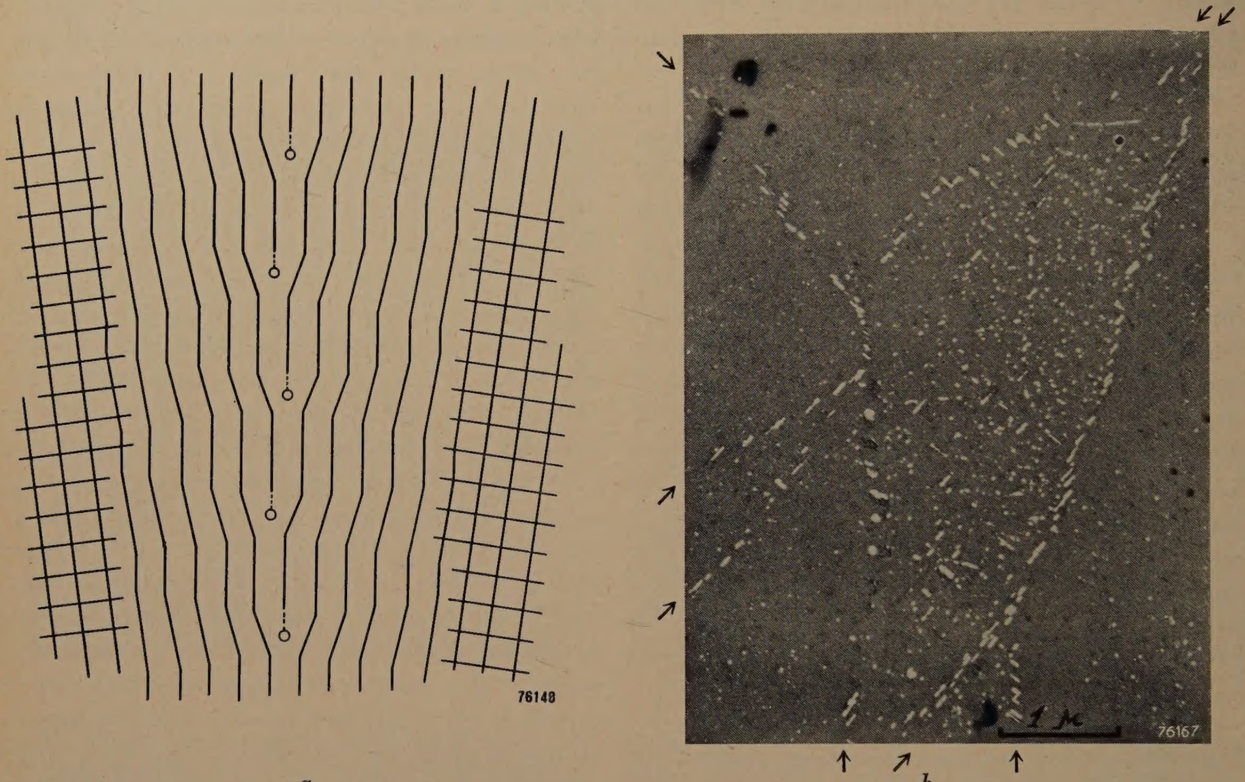
Lastly, we must not overlook the phenomenon of ordering in systems containing more than one kind of atom, say two kinds. Below the so-called transition temperature, a condition is approached in which each atom surrounds itself uniformly with as many as possible of the other kind of atom. In recent years the theory of order-disorder transitions has made great progress by taking into account the interaction of not only nearest atoms, but also their next-nearest neighbours. It appears, for example, from the work of Linde [19]), Mac Gillavry [20]) and Guinier [21]) that in the transition from the state of disorder to that in which order is maintained even over large distances from an atom, contiguous well-ordered zones are formed, the order being disturbed at the boundaries. In the lattice of one zone the atoms are thus disposed in a different manner from that of the atoms in the lattices of neighbouring zones. It again appears as though imperfections at the boundaries which are difficult to eradicate — the so-called stacking faults — must be accepted in order to obtain a reduction in the free energy within the whole space as quickly as possible. This raises the interesting problem that such faults appear to occur only on certain kinds of lattice plane and that this happens at regular distances.

In this connection it is worth while recalling one of Guinier's observations; in an alloy of one atom of aluminium and one of silver he found an ordering of the atoms within short distances, i.e. in very small zones, even though long-distance ordering and a transition temperature have not been found. It may well be that such short-distance ordering occurs in many systems and has some influence on the physical, electrical and also the very susceptible magnetic properties.

The nature of physical lattice imperfections

In the foregoing we have discussed at some length the fact that, for the sake of an increase in entropy and high reaction rates, lattice imperfections occur as a necessary — but none the less interesting — "evil". We have not yet attempted, however, to give any physical picture of the lattice defects.

It is beyond dispute that screw dislocations are a physical reality in the growth of crystals from solutions, and there can also be no doubt as to the accuracy of the picture given in 1939 by J. M. Burgers [22]) of the faults that occur at the crystal boundaries. Means were found to "develop" such faults for examination under light and electron microscopes by making them function as points of nucleation during the formation of new phases [23]) (*fig.* 5). The spacing of the faults thus rendered visible correspond to that anticipated from the known disorientation of adjacent crystals.



a *b*

Fig. 5*a*) Geometrical representation of dislocations at the boundaries between two crystals. (Vide J. M. Burgers, Kon. Ned. Akad. Amst. **42**, 293, 1939.)
b) "Developed" dislocations of the kind depicted in a). The distances are as anticipated from the observed disorientation angle of the adjacent crystals. The arrows indicate the crystal boundaries. (R. Castaing and A. Guinier, Comptes rendus **228**, 2033-2035, 1945.)

Druyvesteyn and co-workers [24]) have for some years concerned themselves with the deformation of metals at low temperatures, and their work makes it probable that, in this case, conforming with the ideas of Seitz, the diffusion of atomic vacancies is in part responsible for the recovery of the lattice after deformation.

In all truth it must be admitted that other kinds of lattice imperfection exist which have never been demonstrated in a fundamental manner, but have been deduced indirectly from various experiments. In physics, where the fundamental experiment generally precedes the theory and the latter precedes the practical application, this is a rather unusual situation. Technological applications based on experience of physical deformation, electrical conductivity and so on, date back a long time. The theory is already in an advanced state of development. Without going into atomic data such as the cohesion between the atoms in a lattice, we have, by geometrical means, constructed models of possible lattice imperfections. In this way the statics of lattice imperfections [25]) and, recently, also their dynamics, have been developed to a high degree and adapted to all the empirically known phenomena. For example, the important new information regarding diffusion, the so-called "Kirkendall effect", has now been added to the applications of the theory of lattice imperfections. Experimentally, however, the fundamental work has so far consisted only of more or less happily chosen models. There is, for example, the well known two-dimensional model of a disturbed lattice devised by Bragg and co-workers [26]) consisting of a "raft" of uniform soap bubbles (*fig.* 6). However, as recently demonstrated by Shockley, it can be very dangerous to derive quantitative data from a model of this kind.

The state of affairs in the field of physical lattice imperfections may be compared with that in the phenomenon of disorder in aggregates of magnetic dipoles, now familiar in ferromagnetism. The latter

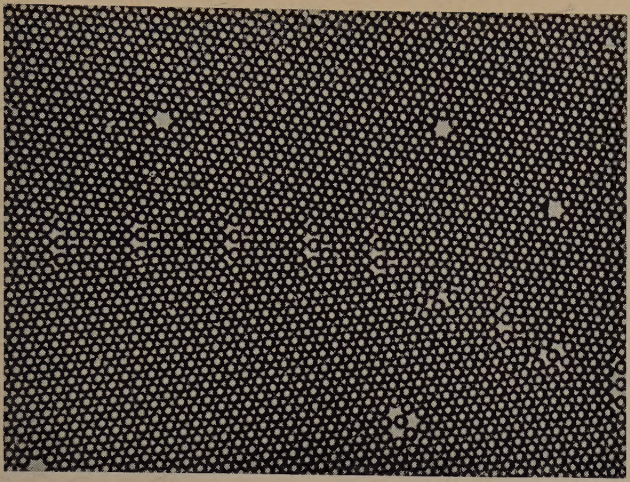


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Fig. 6. Two-dimensional model of an imperfect lattice obtained by drifting uniform soap bubbles against each other (Bragg's bubble method). In this example two "crystals" are seen to have formed with a certain disorientation angle. (W. M. Lomer and J. F. Nye, Proc. Roy. Soc. **A 212**, 567-584, 1952.)

presents a much more favourable picture, partly because many of the phenomena are produced on a very much larger scale. The detailed theory of the geometry of Weiss domains, as given by Néel 27) has been admirably confirmed by experiment. It is to be hoped that in the years to come suitable experiments will enable the present theory of physical lattice imperfections to be verified and applied to the atomic forces at work in a given system.

Regarded superficially, the human body is a beautifully symmetrical structure; yet every surgeon will be able to point out that the internal structure reveals a lack of symmetry that is essential for proper functioning. He would have nothing but admiration for the logic by which these departures from uniformity can be explained. Although, as is usually the case, the analogy is by no means perfect, the physicist, too, studying the imperfect lattice and searching for relationships between the imperfections and many important properties of solids, will be fascinated by the logic of the unfolding pattern and its far-reaching consequences.

Summary. Whereas many of the properties of solids can be explained theoretically on the basis of a model of the periodic space lattice, certain properties and also many phenomena occurring in crystals depend on small departures from the periodicity. The occurrence of such lattice imperfections, in spite of the additional energy required, is shown to be correlated with the increase in the probability of a given state (increase in entropy), or, by the evasion of rate-limiting factors, with an acceleration of changes in structure that are necessary, i.e. which lead to a condition of lower final energy. The first instance is illustrated by a consideration of the interaction between physical and chemical lattice imperfections, for example, in the case of controlled valency substances and in interstitial solutions. The second instance is encountered in phenomena such as the growth of crystals from solutions, segregation, recrystallization and order-disorder transitions, where the processes are in principle determined by the atomic interaction as manifested in nucleation, diffusion, and interfacial tension. Some notes are included on the nature of the lattice imperfections. Although some kinds of imperfection such as screw dislocations, boundary faults, and atomic vacancies are well-known and much theoretical work has already been done on lattice defects, further fundamental work as to the character of all kinds of lattice faults is still required.

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PREPARATION AND CASTING OF METALS AND ALLOYS UNDER HIGH VACUUM

by J. D. FAST, A. I. LUTEIJN and E. OVERBOSCH.

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This article describes a method whereby metals and alloys of extreme purity and precise composition can be produced in a form that lends itself well to further shaping into test specimens or components. The high degree of purity is demonstrated by chemical analysis and in certain instances also by the striking physical properties exhibited by such materials.

In the fundamental investigation of metals and alloys, as well as in their processing and use, many of the difficulties encountered are attributable to impurities which are always present in commercial grade metals. Particularly the so-called structure-sensitive properties of metals are affected by the nature, quantity and distribution of the impurities. Among these properties are mechanical properties such as tensile strength and ductility, and magnetic properties such as permeability, coercive force and hysteresis losses. In order to reveal the optimum values that these properties *can* attain we must be able to produce the metals and alloys in a very pure state and also to add any desired percentage of impurities [1]). By working with alloys of precisely known composition it is also possible to obtain information regarding the very practical questions as to those impurities which are more particularly to be avoided and the probable effect of any divergence from specified percentages of the main constituents. The effect of the latter, when investigated in commercial grade alloys, is often completely masked by the effect of fluctuations in the percentages of impurities.

A few years ago there appeared in this Review a description of an apparatus by means of which metals and alloys of precisely known composition can be prepared by melting them under vacuum, using induction heating [2]). The present article refers to improved equipment which enables an alloy, when once prepared, to be cast immediately in a mould while still under high vacuum. There were two important reasons for designing equipment along these lines, both of which are related to the further processing of the metal. Whether the final product is to be a component or a test specimen, some further shaping operation is usually necessary, — for example forging, rolling, swaging or drawing into wire. During these processes uncontrolled quantities of impurities may find their way into the metal. If the mechanical properties are such that the alloy can be worked at room temperature, the risk of the intrusion of impurities is only slight; the impurities are then confined to a very thin outer layer which can be removed either mechanically or chemically. On the other hand, if the mechanical properties of the alloy necessitate its working at elevated temperatures, impurities are able to penetrate much more deeply. Especially to be feared is the intrusion of elements having small, rapidly diffusing atoms, such as hydrogen, carbon or nitrogen. Particularly with alloys which do not lend themselves well to shaping operations it is therefore important that they should be prepared by casting under vacuum in a shape that will necessitate a minimum of working to reach the ultimate product. The other advantage of casting is that there is a smaller risk of cavities or blow holes than obtains when the melt is cooled in the crucible. Such cavities can be caused by the considerable reduction in volume that usually accompanies the transition from the liquid to the solid state: thus, in the gradual cooling in a crucible, when the interior of the melt remains liquid for some time after the outside has solidified, cavities form as the interior solidifies. By casting in a suitably designed mould, this can generally be avoided, as will be seen presently.

With the experience gained with both the earlier and the present equipment it is now possible to

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[1]) Ordinarily the word "impurity" is held to mean a deleterious constituent, but in this article we shall take it in the wider significance of "a small percentage of alloying constituent", without, however, specifying a sharply defined limit for this percentage. This wider definition has been adopted because it is not a foregone conclusion that all foreign elements are deleterious and because instances occur in which one and the same "impurity" will have an adverse effect on certain properties of an alloy and a beneficial effect on others. — It should also be noted that for the sake of brevity the words metal and alloy are employed in many places as synonyms. This is not unjustified for, strictly speaking, all metals are alloys, as no metals exist in a perfectly pure state.

[2]) J. D. Fast, Apparatus for preparation of metals with an exactly known content of impurities, Philips tech. Rev. **11**, 241-244, 1950.

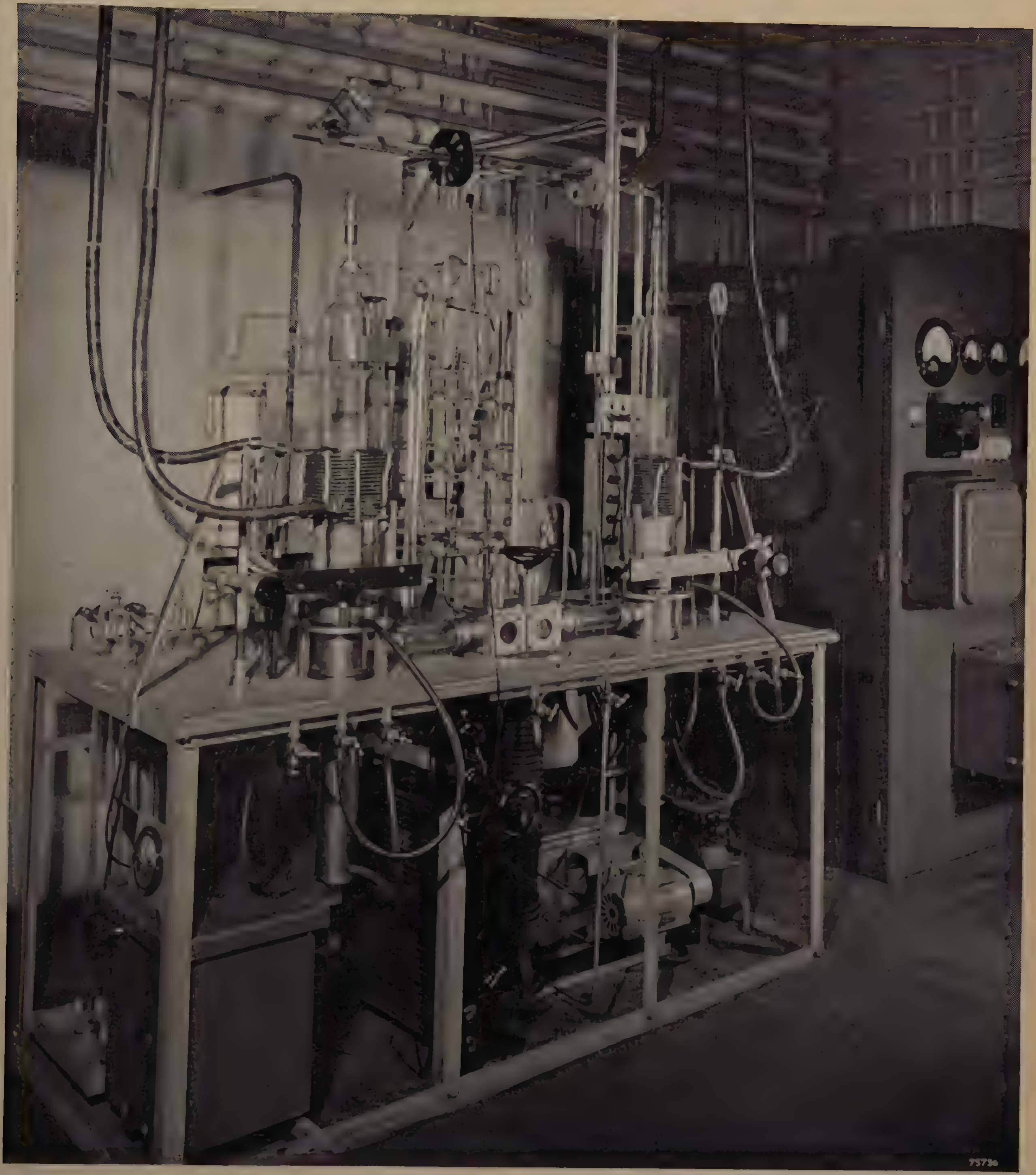

Fig. 1. Melting equipment with two furnaces for melting and casting alloys under high vacuum. The high-frequency induction heating coils are seen in position round the melting chambers. At right (in background) is seen the high-frequency generator (300 kc/s, 25 kW) and, below the bench, the high-vacuum and rotary backing pumps. On the bench, behind the furnaces, will be seen the apparatus for supplying purified gases (hydrogen, argon, oxygen, nitrogen) to the furnaces. Mirrors are mounted above the furnaces to give a clear view of the metal in the crucible.

give a more complete outline of the methods employed in preparing alloys of carefully predetermined composition.

Some examples of the results obtainable by these methods will be given at the end of this article.

Description of equipment

Fig. 1 shows the complete equipment, with the high-frequency generator on the right and the melting apparatus on the left. In the latter, two

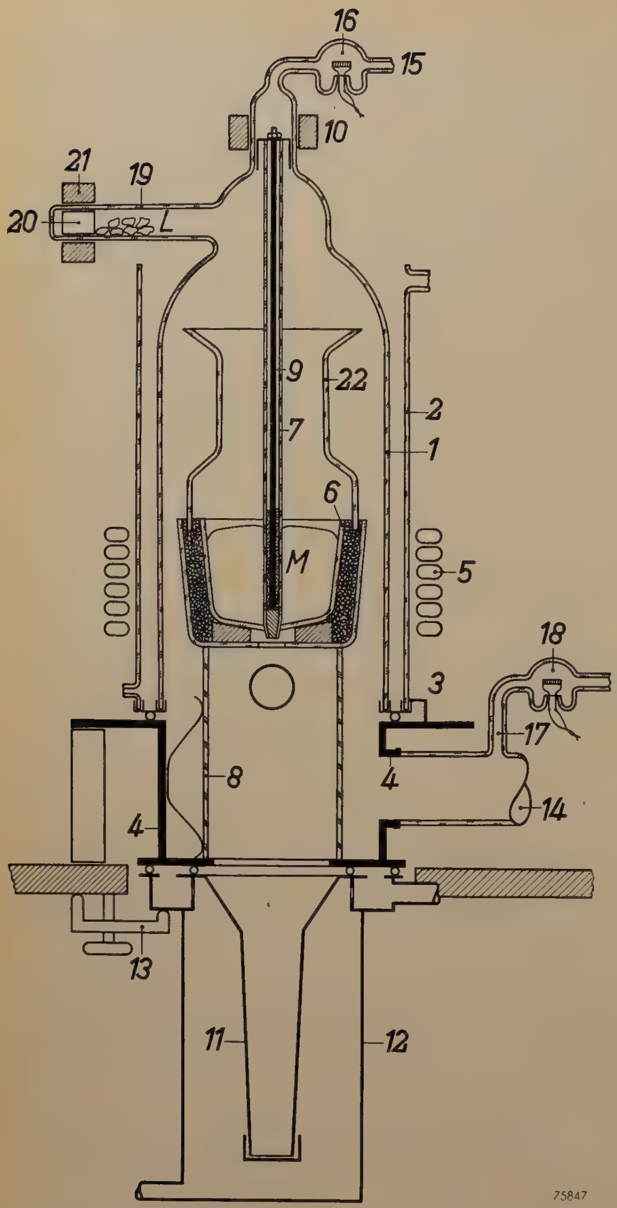

Fig. 2. Diagrammatic cross-section of one of the furnaces (not drawn to scale). The hard glass melting chamber *1* is cooled by the flow of water in the glass jacket *2* and is exhausted through the pumping tube *14*. The metal to be melted (*M*) is placed in a crucible *6* and is heated by high-frequency current in the coil *5*. When the metal has been melted and purified, any required alloying constituents *L* are added from the side tube *19* (pushed out by a ferromagnetic plunger *20*, actuated by a movable solenoid *21*). For casting, the plug *7* is withdrawn by energizing the solenoid *10*. The molten metal then runs out of the hole at the bottom of the crucible into a mould *11*, which is cooled by the flow of water in jacket *12*. Details of construction: the chamber *1* and jacket *2* are mounted on a metal ring *3*, by means of vacuum-tight cement. This ring is held by three clamps on the base *4* of the whole unit; a rubber gasket coated with vacuum grease and lying in a groove in *4* ensures a vacuum-tight joint. The crucible *6* stands on a refractory ring in an outer crucible of quartz, the space between the two being filled with fragments of crucible material. The outer crucible stands on a wide quartz tube *8* which is held in place in the base *4* by means of springs. The plug *7*, which is in effect a ceramic tube, is not attached directly to the ferromagnetic bush within the solenoid *10*, but is carried by a molybdenum rod *9*, this being wedged in the tube by carborundum particles. The metal housing *12* enclosing the mould *11* is held against the base *4* by three clamps *13* with rubber gaskets, to ensure a vacuum-tight seal for the mould and a water-tight seal for the housing. Different gases can be introduced into the chamber through tube *15* and these are removed again through the side tube *17* which is connected to the backing pump. Indicator tubes *16* and *18* serve for checking the oxygen content of the gas; *22* is a quartz funnel.

furnaces will be seen, each of which is fitted with its own induction heating coil.

The pumps used for exhausting the furnaces to a pressure of 10^{-5} mm mercury are housed beneath the bench; they consist of an oil diffusion pump (500 litres per sec.) and a rotary oil backing pump. On the bench may be seen the large metal valves and wide tubes used for connecting the furnaces to the pumps.

Fig. 2 is a diagram of one of the furnaces. The melting chamber proper lies inside a hard glass cylinder (*1*) which is cooled by a continuous stream of water through the jacket (*2*) when melting is in progress. This cooling prevents the liberation of gases from the walls.

At the centre of the chamber is the crucible (*6*) in which the metal is melted. The coil (*5*) for generating the high-frequency electromagnetic field consists of a helix of copper tube, also water-cooled. The coil is mounted outside the melting chamber, so that an alternating current of very high frequency can be used (300 kc/s), ensuring compactness of the equipment [3]). The heat developed in the metal is generated mainly by the eddy currents, but in the case of ferromagnetic metal (iron, nickel, cobalt), hysteresis losses — below the Curie point — contribute towards the heating effect.

The crucible stands on a ring of refractory material in an outer quartz crucible, which is in turn supported by a wide tube of quartz (*8*); this is held in position in a heavy metal base (*4*) by means of three springs. The space between the two crucibles is filled with small pieces of broken crucible material. Both crucibles have a hole at the bottom; the hole in the inner one is closed during melting by a long tube, slightly tapered at the end (*7*) and made of the same ceramic material as the crucible itself. When the metal is ready for casting, this tube is withdrawn; the hole is thus opened and the molten metal flows out into a metal mould (*11*). The tube is lifted by the action of a solenoid (*10*) on a ferromagnetic bush, by means of which the tube is suspended. It is not advisable to attach the ferromagnetic bush directly to the ceramic tube, as the latter would then tend to break easily, especially when the melt reaches a high temperature; for this reason the force is transferred to the tube by a molybdenum rod (*9*) attached to the bush and wedged within the tube by carborundum granules.

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[3]) If the H.F. coil were placed in the melting chamber — which is done in other apparatus (employing lower frequencies) in order to permit *tilting* of the whole furnace for casting — gas discharges between the turns of the coil would occur, owing to the low gas pressures now employed.

The mould (*11*) consists of a slightly tapered copper tube closed at the bottom end with a nut and a suitable vacuum sealing compound; the upper end is flared and terminates in a flange by means of which the mould is attached to the apparatus (with rubber gaskets to ensure vacuum-tightness). The flange rests on the upper channel-shaped rim of the metal casing (*12*): water flowing through the casing and channel effectively cools the mould and gaskets.

The ample cooling of the mould — at least with the simple form of mould depicted (*11*) — ensures that contraction of the metal on solidifying does not result in blow holes: solidification takes place from the bottom upwards, and the shrinkage results only in a crater at the head of the casting (the last part to solidify). The quantity of metal to be cast can be so chosen that the crater occurs wholly within the tapered head of the casting, thus ensuring that the bar itself is solid throughout its whole length.

Melting in a gaseous atmosphere

The melting of the metal prior to casting must often be done in a gas such as argon or hydrogen. The reason for this may be to minimize the evaporation of relatively volatile constituents, but usually — and this refers especially to hydrogen — it is to reduce the oxygen content of the metal as much as possible. Before the gases are passed through the inlet (*15* in fig. 2) into the melting chamber, all residual oxygen is removed by passing them through a purifier (see article referred to in footnote [2])); this consists principally of a tube containing copper chips heated to 500 °C and two coolers, immersed in liquid oxygen when the gas to be purified is argon, or in liquid nitrogen for hydrogen. The purity of the incoming gas is verified by means of a Cr-Ni steel (18/8) indicator tube [4]) (*16*). The gas leaves the melting chamber through a narrow side tube (*17*), passes through another indicator tube (*18*), and escapes through a mercury trap (not shown in the drawing).

Nickel and iron are among the metals from which the last traces of oxygen can be removed by means of hydrogen. The indicator tube (*18*) shows when practically no more oxygen is being released from the molten metal. At this point, however, the metal will contain a quantity of hydrogen in solution in place of the original oxygen. It is just those metals referred to, i.e. nickel and iron, that are much more capable of dissolving hydrogen when liquid, than in the solid state. When casting is effected in hydrogen, therefore, much hydrogen must necessarily be liberated when the metal solidifies. Solidification takes place so rapidly in the water-cooled mould that many gas bubbles are included in the casting. To illustrate this, *fig. 3* depicts an iron bar sawn through after having been melted and cast in hydrogen at 1 atm. (For the normal examination of castings for the presence of blow holes, the castings are of course not sawn through; instead radiograms are taken, in which cavities are revealed as dark spots.)

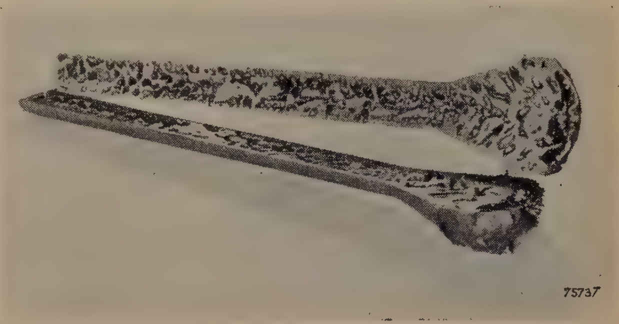

Fig. 3. Iron slug (sawn in half), as produced in the vacuum apparatus after purification and casting in hydrogen at a pressure of 1 atm. Owing to the large volume of hydrogen dissolved, and subsequently liberated by the rapid cooling, the metal is full of blow holes. This can be avoided by pumping away the hydrogen before casting.

The evolution of gas during solidification can be completely prevented by pumping away the hydrogen after purification; in fact, if the gas is pumped away until a pressure of 10^{-3} mm mercury is reached, a cast bar of purified iron shows no trace of blow holes or porosity at all. It is necessary to commence pumping slowly, as the dissolved gas otherwise escapes with such violence that drops of metal are entrained by the gas. To prevent this, the melting chamber is first connected to the backing pump by means of a cock in the narrow tube (*17*); when the greater part of the gas has been removed, the wider tube (*14*) to the main pump is opened and the pressure is reduced to below 10^{-3} mm Hg in a matter of minutes. This pressure is measured at the main inlet tube (*15*), to ensure that the pressure in the melting chamber is not actually in excess of the value measured.

If the required alloy is to contain elements that have a high affinity for oxygen (e.g. aluminium, zirconium, titanium, vanadium) it is better not to add these to the other metals in the crucible from the start as, during the melting process, they then combine with the oxygen present in the iron, nickel, etc. The oxides thus formed, viz. Al_2O_3, ZrO_2 etc., cannot be reduced with hydrogen. It is true that these oxides coagulate and, owing to their higher or lower specific gravity compared with that of the melt, will either sink to the bottom or rise to the surface. However, in practice, this coagulation and separation take places very slowly. It is therefore better to add the above-mentioned "impurities" to the melt only when those constituents which can be reduced with hydrogen have been fully purified. The materials to be added are placed in a side tube (*19*), and at the appropriate moment they are introduced into the melt by means of a ferromagnetic plunger (*20*) actuated by a movable solenoid (*21*). The special shape of the transparent quartz funnel (*22*) ensures that the metals fall into the crucible. This funnel also fulfils other important functions, such as protecting the glass wall of the melting chamber from spattering metal, and condensing the greater part of the evaporated metal.

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[4]) G. W. Rathenau and H. de Wit, Metallurgia **40**, 114, 1949.

Some further general points concerning the preparation of very pure alloys will now be mentioned.

Choice of raw materials

For making alloys of high purity it is obviously necessary to select very pure ingredients. It should be remembered that all metals qualified as "pure" nevertheless contain a certain quantity of unspecified impurities. This applies also to "spectrochemically pure" metals, since spectrochemical analysis, apart from its limited (albeit high) sensitivity, does not usually give any indication of the presence of carbon, nitrogen, hydrogen, phosphorus or sulphur; these elements, even in very small concentrations, generally have unexpectedly pronounced effects on the properties of a metal or alloy. For example, a small percentage of sulphur in nickel is so detrimental that for many applications a nickel containing 0.01% of sulphur, which might indeed be termed "spectrochemically pure", would actually be regarded as highly impure and useless for the purpose (see *fig. 4*). In contrast, nickel containing 0.1% of cobalt may for the same purpose be considered fairly pure and quite usable.

This implies that when a choice is to be made from different qualities of a metal, it is not always the metal with the lowest total content of impurities that will be selected. If the impurities are such that they can be eliminated during the melting process only with difficulty, or not at all (and this includes cobalt and sulphur in nickel), the choice will depend on the harmfulness of the impurities present, from the standpoint of the particular characteristics or application in mind. Also, where the choice lies between alternative impurities *A* and *B*, the first of which is very difficult and the second relatively easy to eliminate during the melting process, a sample containing a large quantity the impurity *B* might be preferred to one containing only a small percentage of *A*. For instance, the best electrolytic iron is of much higher purity than the best carbonyl iron, but the latter contains almost only carbon, oxygen and nitrogen as impurities, which can be removed during melting (see article referred to in footnote [2])), whereas electrolytic iron is liable to contain metallic impurities that cannot be removed easily, if at all.

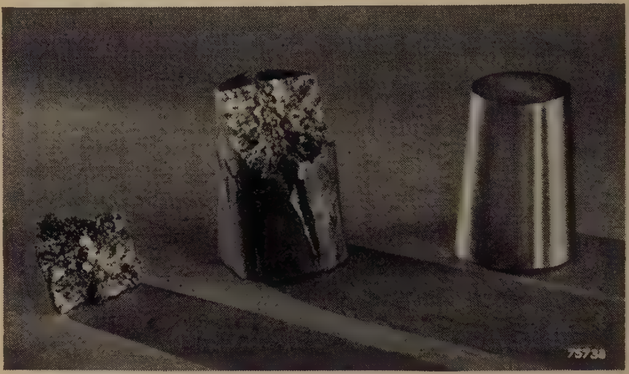

Fig. 4. Test specimens of nickel containing 0.02% sulphur, as obtained by solidification in the crucible (i.e. without casting). A specimen of this kind would have to be processed to give it the desired form by forging, rolling, drawing etc,, but, owing to the sulphur, the metal was too brittle to permit any deformation. The result of an attempt to forge this material is seen in the specimen at the left of the photograph.

Metallic impurities are eliminated without difficulty when the volatility of the basic metal is much lower than that of the other metals. For instance, in the equipment described, which can be exhausted to a pressure of 10^{-5} mm mercury, the manganese content of iron can be reduced to less than 0.001% by volatilization from the molten iron at 1600 °C.

In principle, metallic impurities of which the affinity for oxygen is much greater than that of the basic material can be eliminated by allowing the molten mass to absorb a controlled amount of oxygen; the impurities then undergo preferential oxidation. It has already been pointed out, however, that the oxides formed usually separate from the metal very slowly: for this reason this method of purification is not very practicable.

Effect of the crucible

Although the melting process offers facilities for removing many impurities from an alloy, the possibility of the introduction of impurities from the crucible itself must always be considered. The choice of crucible material is therefore very important [5]). Generally speaking, it is necessary to employ *ceramic materials* for this purpose.

Metal crucibles are not usually suitable, since nearly all metals form alloys with each other. Iron and lead form an interesting exception. Iron is virtually insoluble in lead, so that lead can be melted in an iron crucible without contamination by the crucible itself.

In exceptional cases graphite crucibles can be employed, viz. for melting copper. In most cases, however, graphite is unsuitable for crucibles, as many metals tend to form carbides with the walls, or at any rate to dissolve appreciable quantities of carbon from them.

For the highly reactive metals titanium and zirconium there is in fact no crucible material that will give entire satisfaction. With graphite crucibles, contamination by the carbon is anything but negligible, and ceramics are not suitable because these metals in the molten state cannot be brought into contact with any oxides (even their own) without dissolving large quantities of oxygen. The graphite crucible in this case appears to involve the lesser of the two evils.

A material much employed for crucibles is pure aluminium oxide and, for a long time, mainly this material has been used in this laboratory. It is important to note, however, that this may not always be the most suitable ceramic material. Thus, if an alloy containing carbon is melted in a crucible of pure aluminium oxide, it will take up metallic aluminium as an impurity, as a result of reaction between the carbon and the crucible material. Even in the case of carbon-free metals, the use of crucibles of Al_2O_3 can lead to the appearance of Al in the melt; the following equilibrium is established:

$$Al_2O_3 \rightleftarrows 2[Al] + 3[O]\,, \quad . \ . \ . \ . \quad (1)$$

in which the square brackets denote the components dissolved in the molten metal. The partial dissociation of the solid Al_2O_3 as indicated in (1) must not be entirely disregarded, for example, when the melt is of iron, because of the high heat of solution of aluminium and oxygen in molten iron. The thermodynamics of this reaction show that the reaction constant at a temperature of 1600 °C is given by:

$$K = [\%\,Al]^2 \cdot [\%\,O]^3 \approx 10^{-13}, \quad . \ . \quad (2)$$

where the quantities within the square brackets are the percentages by weight. The purification of carbonyl iron (see above) may be cited as an example: the iron is subjected to prolonged heating at 1600 °C, in an atmosphere of pure hydrogen. If the iron is contained in an Al_2O_3 crucible, the equilibrium illustrated above will be established and, in accordance with (2), the Al content of the iron will rise according as the oxygen content drops. If the oxygen content of the molten metal be reduced to 0.001%, the melt, according to (2), will take up about 0.01% Al from the crucible.

Iron of greater purity can be obtained by using a crucible made of *magnesium oxide*. Since the heat of solution of magnesium in molten iron is opposite in sign to that of aluminium, the reaction constant of the equilibrium corresponding to (1) is much smaller than that given by (2). Moreover, magnesium is much more volatile than aluminium, and the magnesium formed during the process leaves the molten iron by evaporation.

Typical analyses of carbonyl iron with purification in Al_2O_3 and MgO crucibles will be found in *Table I.*

The electrical resistivity at low temperatures is a very reliable indication of the purity of a metal; the purer the metal, the lower this "residual resistance". To obtain some idea of the order of magnitude of this residual resistance, the electrical resistance R at 291 °K (room temperature) may be compared with that at 20 °K (temperature of liquid hydrogen). For iron melted in an Al_2O_3 crucible the ratio R_{291}/R_{20} was found to be 31. The iron melted in an MgO crucible yielded a ratio of 140, and this high value (as also Table I) illustrates the very high purity of MgO iron.

Table I. Percentages of impurities in iron melted in the vacuum apparatus in two different crucibles.

	Al_2O_3-crucible	MgO-crucible
Mg	0.000^7%	0.001^6 %
Si	0.002	0.002
Al	0.027	0.001
Cu	0.002	0.000^5
Co	0.001	0.000^5
Ni	0.006	0.003
C	0.000	0.000
S	0.000	0.000
O	0.000	0.000

Applications of the method

The preparation of pure iron in an MgO crucible, as described above, is representative of the high degree of purity obtainable with this apparatus. Taking this pure iron as a starting point, investigations have been made on the individual influence of various impurities of practical importance upon

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[5]) Not long ago a description was given of a method of melting metals in a freely suspended state, i.e. not in contact with a crucible; see E.C. Okress, D. M. Wroughton, G. Comenetz, P. H. Brace, J. C. R. Kelly, Electromagnetic levitation of solid and molten metals. J. appl. Phys. **23**, 545-552, May 1952. So far, however, this method has been developed only for very small quantities of metal.

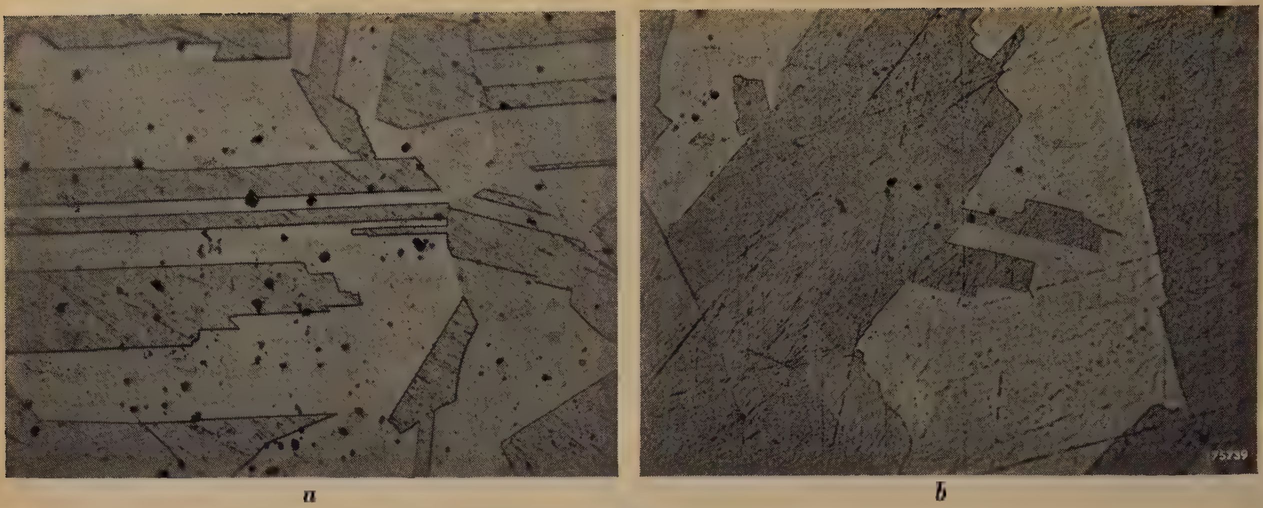

Fig. 5. *a*) Photo micrograph of an alloy of 80% Ni + 20% Cr prepared in accordance with conventional methods.
b) Photo micrograph of the same alloy prepared in the vacuum apparatus. It is at once evident that this contains much fewer inclusions than the specimen in (*a*). Owing to the greater purity of this specimen compared with (*a*), etching for a longer period was necessary to render the grain boundaries visible. The longer etching is evidenced by the more pronounced scoring of the polished surface. Magnification of (*a*) and (*b*) 400 ×.

the characteristics of the iron; the effects of certain combinations of impurities have also been studied. The results of these experiments have already been published in this journal and elsewhere [6]), and further results will be given in the near future.

Many nickel alloys of exceptional purity have also been prepared in the vacuum apparatus. Some examples are given below.

1) *Figures 5* and *6* are photo micrographs of alloys of 80% Ni + 20% Cr, the one alloy prepared in accordance with conventional methods and the other in the vacuum apparatus. It is clearly seen that the last-mentioned alloy contains much fewer inclusions than the first.
2) A high degree of purity, and in particular the absence of inclusions, is essential in alloys which are to be magnetically "soft". *Fig. 7* shows the

Fig. 6. Photo micrographs taken with "dark ground" illumination (light at grazing incidence) of the same alloys as in figs. 5*a* and *b*. By this method of illumination the polished, specularly reflecting surface of the metal is invisible, but the irregularities caused by the inclusions appear as bright points. *a*) Alloy prepared in the usual manner; *b*) alloy made in the vacuum apparatus. Magnification 550 ×.

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[6]) J. D. Fast, Investigations into the impact strength of iron and steel, Philips tech. Rev. **11**, 303-310, 1950; J. D. Fast, Ageing phenomena in iron and steel after rapid cooling, Philips tech. Rev. **13**, 165-171, 1951; J. D. Fast and L. J. Dijkstra, Internal friction in iron and steel, Philips tech. Rev. **13**, 172-179, 1951; J. D. Fast, Strain ageing in iron and steel, Philips tech. Rev. **14**, 60-67, 1952; J. D. Fast and J. L. Meijering, Anelastic effects in iron containing vanadium and nitrogen, Philips Res. Rep. **8**, 1-20, 1953 (No. 1); J. D. Fast and M. B. Verrijp, Diffusion of nitrogen in iron, J. Iron and Steel Inst. to be published shortly.

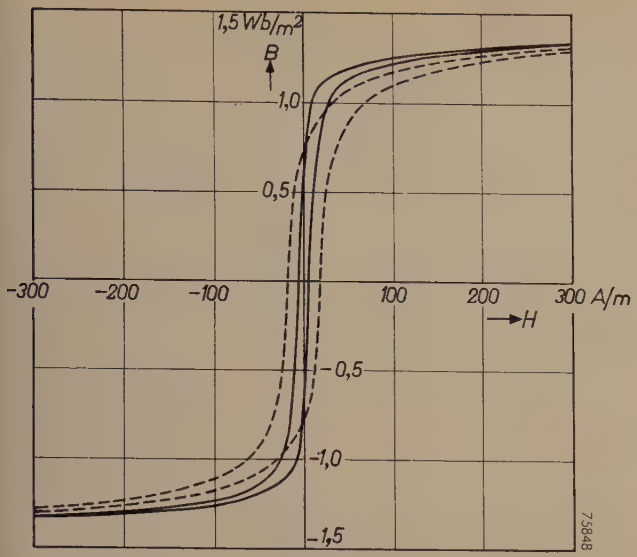

Fig. 7. Magnetization curve of two alloys of 40% Ni + 60% Fe. The broken lines relate to an alloy carefully prepared along conventional lines; the coercive force is as low as any value for such alloys mentioned in the literature [7]). The full line refers to an alloy prepared in the vacuum apparatus.

BH curves of two alloys of 40% Ni + 60% Fe; the full line refers to an alloy made in the vacuum apparatus, and the broken line to an alloy prepared with the greatest care along conventional lines. The coercive force of the last-mentioned metal is 16 A/m (0.2 oersted), which corresponds to that of the best alloys of this composition mentioned in literature on the subject [7]). The alloy made in the vacuum apparatus has an appreciably lower coercive force, viz. 3.2 A/m (0.04 oersted). In each case the heat treatment preceding magnetic measurement was the same; the specimens were made in the form of a ring (produced by rolling the cast bar to a flat plate and then turning on a lathe) and were heated together for 5 hours at 1200 °C in pure hydrogen.

3) The purity of alloys prepared in the vacuum apparatus was also demonstrated in the making of Al-Ni alloys containing about 1 atom Al to 1 atom Ni, as well as in alloys of this composition, to which small quantities of another metal, e.g. iron had been added. These alloys were all of a bright metallic colour and did not exhibit variations in tint observed by other research workers [8]). This seems to point to the fact that the coloration is attributable to impurities which can be avoided by preparation in the vacuum apparatus.

In accordance with what has already been said in the preceding section, the pure chromium and aluminium used for the alloys in experiments (1) and (3) were first placed in the side tube *19* of the apparatus (fig. 2). They were added only after purification of the molten nickel in a stream of hydrogen. In view of the great heat of reaction between aluminium and nickel, the former had to be added in small portions. Only when all the metal had been added was the hydrogen pumped off and the alloy cast in the mould.

The importance of the preparation of pure alloys for metallurgical research has already been demonstrated. It may, however, be interesting to note that the vacuum melting apparatus can also be usefully employed in the development and manufacture of certain new products. In many cases the importance of alloys prepared in this manner lies not only in their precisely determined and possibly unconventional composition, but also in the fact that alloys melted and cast under high vacuum liberate very little gas when subsequently heated in the solid state. This is a very essential property for many of the components used in electron tubes, especially the lead-in wires through the glass envelope. Gas liberated by the internal components tends to reduce the life of the tube, while gas produced by the lead-in wires or plates may result in leaky seals. During the development of new types of electron tube so many unpredictable factors are operative, that it is a great advantage to be able to exclude one of them, viz. the harmful effects of evolved gases. The apparatus described in this article, which will handle charges up to about 2 kg, can even be used for production on a factory scale for certain components. This is the case for certain components which require only small quantities of metal in each tube (for example in the form of very thin wire) the cost of the material is of minor importance.

Summary. By melting metals and alloys under a high vacuum it is in many cases possible to attain a very high state of purity. Risk of introducing impurities into the pure alloy during processing is minimized by casting, also under high vacuum, in a cooled mould of suitable form. This simultaneously avoids the blow holes which normally occur when charges of several kilogrammes are cooled slowly in the crucible. The apparatus designed for this method of making castings is described in detail. Some points of practical interest with regard to the choice of the ingredient metals and crucible are also given. A few examples are included to demonstrate the high purity of the alloys prepared in the apparatus described; such alloys are particularly useful for metallurgical research, as well as for the development of electron tubes and other products.

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[7]) Cf. R. M. Bozorth, Ferromagnetism, Van Nostrand Co. New York, 1951, fig. 5-14, p. 115.
F. Pawlek, Magnetische Werkstoffe, Springer Berlin, 1952, fig. 158, p. 188.

[8]) A. J. Bradley and A. Taylor, Proc. Roy. Soc. A **159**, 56-72, 1937.

THE DETERMINATION OF DROPLET SIZE IN ARC WELDING BY HIGH-SPEED CINEMATOGRAPHY

by P. C. van der WILLIGEN and L. F. DEFIZE.

621.791.75:778.534.83

In arc welding, material is transferred from the welding electrode to the work in the form of droplets. To a certain extent the size of these droplets determines the welding characteristics of the electrode. In order to provide data regarding the droplet size, films have been made of the transfer of the weld metal, with a camera taking up to 3000 frames per second. With the same camera, colour films have also been made which present a very clear picture of the welding process as a whole.

Introduction

Investigation into the manner in which the metal is transferred from the welding electrode to the work in arc welding, has revealed that this usually takes place in the form of free droplets of molten metal. Sometimes the droplets are so large that they constitute a short circuit while flowing from the electrode into the pool — in this case the droplets can no longer be considered to be wholly free.

To a great extent the droplet size determines the welding characteristics of the electrode; it is known that small droplets result in a smooth bead, and that the smaller the droplet, the more stable the arc. This stability relationship is especially noticeable in A.C. welding, where the arc is established twice per cycle. Electrodes producing small droplets, moreover, melt more quickly than those which give the larger drops, because a large drop usually clings to the electrode for a relatively longer time, thus impeding the melting of fresh weld metal. On the other hand the welder will generally prefer to employ an electrode giving a large drop when it is required to span the gap between two plates.

The number of different kinds of electrode manufactured has gradually increased in the course of time, and the need has arisen for a quantitative determination of the droplet size occurring with the various electrodes. In order to meet this need, systematic measurements have been carried out in the Philips laboratories at Eindhoven, and a description of the method employed is now presented. To illustrate the results obtained, the oxide-silicate and gas-shielded electrodes will be compared with the "contact" electrode which was derived from these types [1]). The results obtained with a "basic" or low-hydrogen electrode are also mentioned.

Before low-hydrogen and contact electrodes were introduced (the first of these before, and the second just after the last world war), mild steel and low-alloy steels were welded almost exclusively with oxide-silicate or gas-shielded electrodes, of which the Philips 50 and Philips 48 are examples.

Basic electrodes are so named because the main constituents of the coating are basic oxides. The outstanding feature of this kind of electrode is that the coating gives off very little water vapour which otherwise produces atomic hydrogen in the arc; this is liable to be absorbed by the molten metal, with detrimental effects on the weld [2]). These low-hydrogen electrodes excel by reason of their good mechanical properties and low sensitivity to impurities (especially sulphur) in the metal to be welded. However, they have to be used with a very short arc if porous welds are to be avoided, and this imposes rather heavy demands on the skill of the welder.

Contact electrodes are noted for their easy welding, and more particularly, for their high welding speed [3]). They do not represent a new type of electrode in the sense that the coating yields a new kind of slag, i.e. one not met in other kinds of electrode. Their essential feature lies rather in a modification of existing types, to produce an electrode suitable for contact welding, i.e. the arc is struck automatically when the coating is brought into contact with the work; the electrode with its coating is then rested on the work while the weld is being made. To make this possible, a semi-conductive coating is used, which is also thicker than usual, owing to the fact that a large part of the core metal is included in the coating in the form of powder.

Method of measurement and apparatus used

In order to determine the size of the droplets, films have been made of the arc, a method often employed to demonstrate the transfer of the weld metal from the electrode to the work. It was already known that the processes taking place within the arc are so rapid that very high film speeds (> 1500 frames per sec) would be required to permit these processes to be followed [4]). Use was made of an Eastman high-speed camera type III, which is capable of taking a maximum of 3000 frames per sec. on 16 mm film; exhibited at the normal speed of 24 frames per sec. the pictures are seen slowed down by a factor of up to 125. The camera does not of course operate at full speed from the moment of starting; this speed is developed in accordance with the curve shown in *fig. 1.*

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[1]) For a review of the characteristics and composition of welding electrodes see for example J. D. Fast, The function of the coating of welding rods, Philips tech. Rev. **10**, 114, 1948.

[2]) J. D. Fast, Low-hydrogen welding rods, Philips tech. Rev. **14**, 96, 1952 (Nos. 3-4).

[3]) P. C. van der Willigen, Contact arc-welding, Philips tech. Rev. **8**, 161, 1946 and **8**, 304, 1946.

[4]) A. Hilpert, Werkstoffübergang im Schweisslichtbogen, Z. Ver. dtsch. Ing. **73**, 798-799, or Welding J. **8**, 21, 1929 and **12**, 4-8, 1933.

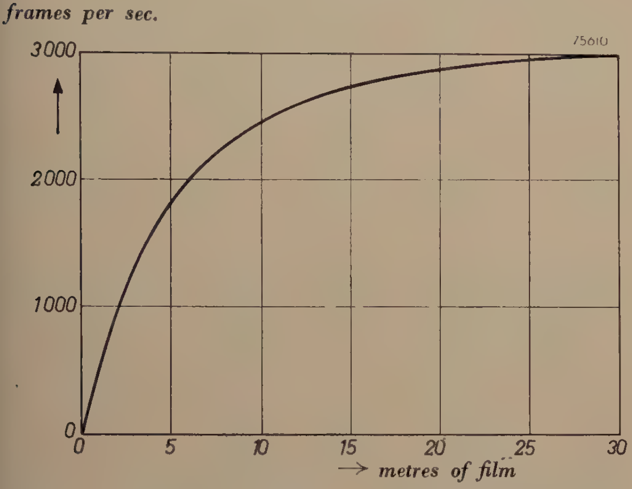


Fig. 1. To determine the diameter of the droplets transferred from welding electrode to work, a cine camera taking up to 3000 frames per sec was used. The curve in the diagram shows how the speed develops after the camera is started.

To obtain an indication of the speed relating to every part of the film, 50-cycle A.C. was used for the welding arc; the current thus passes through zero 100 times per second, so that the arc extinguishes that number of times per second. Another argument in favour of filming an A.C. arc is the increasing use of the A.C. welding technique, which involves much less difficulty due to magnetic arc blow and requires less expenditure on equipment.

The fumes, as well as the light emitted by the arc, tend to make filming difficult. The fumes can be blown from the field of view by means of a current of air directed across the arc. To minimize the effect of too much light from the arc itself, a powerful light source was placed behind it (*fig. 2*); originally a 60 A arc lamp from a cinema projector was used, the light being concentrated around the welding arc by a concave mirror, to produce a background of high and constant brightness [5]). The welding arc thus became almost invisible against the background, and the droplets of molten weld metal could be filmed in silhouette.

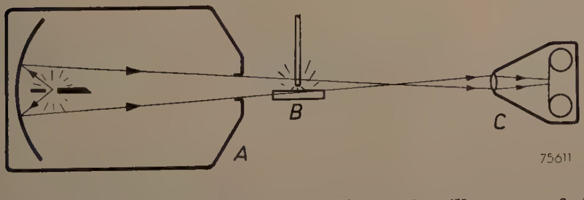
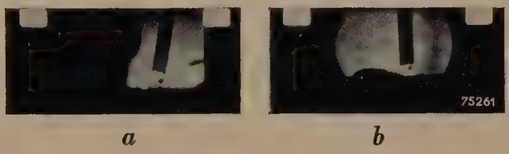


Fig. 2. Diagram of set-up for the filming in silhouette of the weld metal droplets in the welding arc. The light from a carbon arc lamp *A* is concentrated in the welding arc *B* by a concave mirror, so that the droplets can be seen against a bright background. *C* camera.

However, this light source was cumbersome and proved rather unmanageable in use, and it was subsequently replaced by a water-cooled mercury vapour lamp, this being much more convenient to handle. To concentrate the light, a lens was mounted between the lamp and the arc. Another advantage of this type of light source is that it introduces no interfering objects in the beam; the carbon arc and mirror had to be very carefully watched, to ensure that no shadow from the carbon-holder fell across the welding arc (see *fig. 3*).

Fig. 4 depicts the actual apparatus used, with the mercury vapour lamp. The welding electrode was mounted in such a way that the arc remained in the same place while the electrode was being consumed, with the electrode-holder lying in the direction of the electrode itself and supported by four guide rollers. The work was pulled along below the arc at the required speed by an electric motor. It was not found necessary to use automatic feed for the electrode-holder to maintain a constant arc length.



a *b*

Fig. 3. Increase in the field of view obtained by replacing the arc and mirror by a high-pressure mercury vapour lamp in the apparatus depicted in fig. 2.
a) Field with carbon arc and mirror. The shadow of one of the carbon-holders is visible on the left.
b) With the mercury vapour lamp the shadow is eliminated. The silhouette of the small bead already deposited can be clearly seen.

The arc length was checked by means of an optical system with calibrated eye-piece, and the camera was started as soon as the arc attained the desired length. The operator hat no difficulty in keeping the arc length constant for the few seconds needed to take the shot (15 m of film).

Another very attractive method of photographing the welding process is by means of X-rays [6]), the advantage of

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[5]) A similar arrangement was first employed by L. Bull; see M. Lebrun, La soudure électrique à l'arc et ses applications, Bibl. off. centr. acétylène et soud. autog., Paris, 1931, pp. 39-44.

[6]) J. Sack, A new method for the investigation of the transfer of material through the welding arc, Iron and Steel Inst. Symp. on the welding or iron and steel, part 2, 553-559, London, 1935. J. Sack, Welding and welding rods, Philips tech. Rev. 2, 129, 1937.

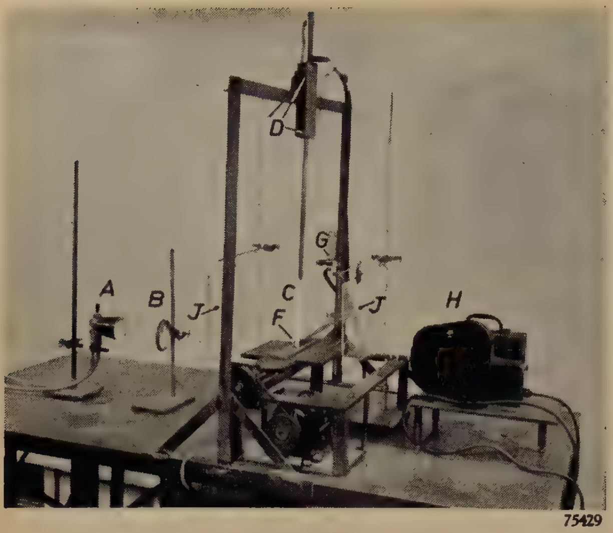

Fig. 4. Actual apparatus employed for filming the transfer of weld metal in the welding arc. *A* water-cooled mercury vapour lamp, the light from which is concentrated on the welding arc by a condenser lens *B*. *C* welding electrode (whitened with chalk to distinguish it from the holder). *D* insulated rollers between which the electrode-holder passes. *E* motor for drawing the work slowly under the arc. *F* jet (16 × 5 mm) through which 20 litres of air per minute is blown, to disperse the smoke laterally. *G* gauge indicating air velocity. *H* cine camera (up to 3000 frames/sec). *J* vertically mounted glass plates for protecting camera and condenser from spattering metal.

this being that it is thus possible to distinguish between the coating or slag and the metal. Further, no difficulties are then encountered owing to the light from the welding arc, or with fumes, so that it is not necessary to take steps to counteract these. As far as we are aware, however, no equipment has so far been designed that will give cinematographic X-ray pictures of sufficient frame speed. At the same time, efforts are being made to increase frame speed in X-ray filming techniques, for instance, Slack and co-workers [7]) describe a camera that will take 150 frames per second.

In order to obtain comparative data of the droplet size, it would be sufficient to have available a large number of instantaneous pictures, not necessarily in the form of film; the slow-motion film, however, does provide an opportunity for studying the whole process of droplet formation, the transfer of the weld metal and the form and motion of the arc.

Determination of characteristic droplet size

The individual pictures of the film are projected one by one on the screen, from which the diameters of the droplets as well as the diameter of the electrode are measured. As the actual electrode size is known, the real diameter of the droplets is easily ascertainable.

It is first necessary, however, to define the size of the droplet to be regarded as *characteristic* of an electrode. The transfer of metal is determined by the *volume* of the droplets, so it is desirable to work in terms of droplet volumes as obtained from the observed diameters. Let n_i be the number of droplets found of which the volume is v_i. It will be clear that the arithmetic mean droplet volume $\Sigma n_i v_i / \Sigma n_i$ will not be suitable for representing the volume of the characteristic droplet. As against the very large number of small droplets, the influence of the larger drops, which, after all, are those that contribute most towards the transfer of metal, would thus remain obscured [8]). This objection is removed by counting each drop a number of times proportional to its volume, i.e. to the contribution of the droplet to the transfer of weld metal. The characteristic droplet volume is then defined as:

$$v_c = \frac{\Sigma n_i v_i^2}{\Sigma n_i v_i}.$$

Now each droplet is encased in a protective coating of slag [9]), and the volumetric percentage of slag will certainly vary between one droplet and another. However, in order to take the average volume of slag into account in the calculation, we reduce the characteristic droplet volume by the (known) volumetric percentage of slag in the molten bead, taking the result to be the characteristic volume of the iron core of the droplets. From this we then obtain the *characteristic diameter* d_c of the droplet core.

As an example, *fig. 5* shows a histogram of the number of observed droplets as a function of their

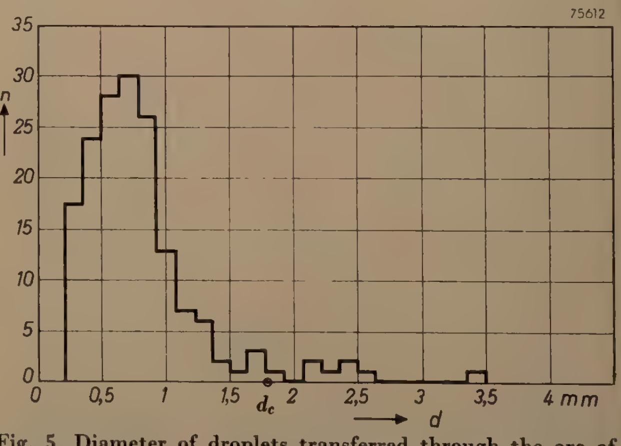

Fig. 5. Diameter of droplets transferred through the arc of contact electrode C 18-4, used with free arc. Vertical axis: number of droplets whose diameters lie between the limits defined by the intervals (1/7 mm in width) on the horizontal axis. (Here the characteristic diameter d_c of the core of the droplet is 1.8 mm). For the measurement, the film was projected with an enlargement of 7×. Droplets of smaller diameter than 3/14 mm (1.5 mm on the screen) could not with any certainty be distinguished from blemishes in the film, and are therefore not included.

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[7]) C. M. Slack, L. F. Ehrke, D. C. Dickson, and C. T. Zavales, High speed cine-radiography, Non-destr. Test., Spring 1949, pp. 7-11.

[8]) Some of the metal evaporates. Strictly speaking, all the metal atoms in the vapour should also be taken into account as separate droplets, but this number of atoms is so large that the average droplet volume would be almost equal to the volume of a single atom.

[9]) See articles referred to in footnote [6]).

diameter, for the contact electrode [10]), C 18-4 (with which 38% of the total volume of the bead of molten material is slag). Another complication is encountered with contact electrodes in that the size of the droplet cannot be determined from the silhouette if the weld is made in accordance with usual practice. Normally, the cup of the electrode rests on the work, and the space between the coating and the work is then so small that the formation of the droplets cannot be observed. To enable the droplet size to be determined, the welding with the contact electrode was therefore done using an open arc. It remains a moot point whether the size of the characteristic droplet in the normal contact welding procedure would be the same.

The values obtained for contact electrodes C18-4 and C20-4, as well as for the oxide-silicate electrode Philips 50-5 (from which contact electrode C20 was derived), are shown in the *table*. A few of the results of measurement on the basic (low hydrogen) electrode Philips 56-5 are also included.

Table. Diameter of the iron core of the *characteristic* droplet for several types of welding electrodes.

Electrode	Current (amp.)	Arc voltage (volt)	Arc length (mm)	Drops per sec.	d_c (mm)	d_c/D	d_c/D' (for contact electrodes)
C 18-4	180	45	4.8	185	1.9	0.47	0.41
,,	180	47	6.6	133	2.0	0.50	0.44
,,	165	42	6.1	145	1.8	0.44	0.38
C 20-4	190	35	6.1	91	2.3	0.58	0.44
Philips 50-5	200	35	4.8	162	1.3	0.26	
Philips 56-5	230	37	8.0	29	2.7	0.54	
,,	230	37	6.2	32	2.8	0.56	
,,	230	38	5.3	42	3.3	0.66	
,,	200	38	5.5	24	2.6	0.53	

In general, larger droplets are to be expected to result from larger core diameters D, so that, to characterise the type of welding rod, the value of d_c obtained should be divided by the value of D. For the contact electrode, moreover, the ratio d_c/D' is also given, where D' is the core diameter which the contact electrode would have if all the iron in the coating were included in the core. (In the C18, 24% of the iron is in the coating as powder; in the C 20, 41%.)

Discussion of results

The gas-shielded electrode Philips 48 was specially designed to give a large droplet, and the film in fact showed that metal was transferred from this electrode only when the arc was short-circuited (*fig. 6a* and *b*). It is therefore somewhat surprising that with the C18 electrode, which is the contact version of the Philips 48, the material is transferred only in the form of small, free, droplets (fig. 6*c*). The conversion to contact electrode has thus resulted in an appreciable decrease in the size of the droplet. Just the opposite has taken place, however, in the oxide-silicate electrode Philips 50 and its contact counterpart, the C20; the table shows that the ratio d_c/D' of the C20 is almost twice the ratio d_c/D of the Philips 50. No explanation has as yet been found for these facts.

The ratios d_c/D' of the C18 and C20 electrodes are practically the same. It is remarkable that a much larger percentage of very small droplets was found for the C18 than for any other of the electrodes measured. In the calculation of d_c, however, these smaller droplets are of minor importance.

The molten metal at the extremity of the Philips 50 electrode, as well as that in the metal pool, is very mobile. This fact, coupled with the smallness of the droplet (the smallest measured) is related to the comparatively high FeO content of the molten metal (approx. 0.04%), which greatly reduces the viscosity and surface tension of the molten metal. The droplets transferred are irregular in shape.

The Philips 56, low-hydrogen electrode gives the largest droplets (figs. 6*d* and *e*); the spherical form of the droplet is characteristic of this electrode. It is known that the FeO content of the weld metal of this basic electrode is very low (0.001%); the viscosity and surface tension are accordingly high.

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[10] The second figure in the designation of an electrode in every case indicates the core diameter in mm.

Sack[11]) has also measured the droplet size of the Philips 50-5 and 48-5 electrodes, in this case by welding rapidly over a copper plate, so that the droplets were caught separately. These droplets, from which the slag was removed, were sorted according to weight, and the characteristic diameters of the droplets computed along much the same lines as those described above. For the Philips 50-5 electrode, Sack obtained a value of $d_c/D = 0.7$, which is roughly twice the value found by us. It is very probable, however, that by this method the droplets obtained are not droplets in the true sense, but larger masses formed by the merging of several droplets before solidification. For the Philips 48-5, Sack obtained droplets for which $d_c/D = 0.9$, but the method employed by him does not really lend itself to revealing whether the transfer of material is accompanied by shorting of the arc.

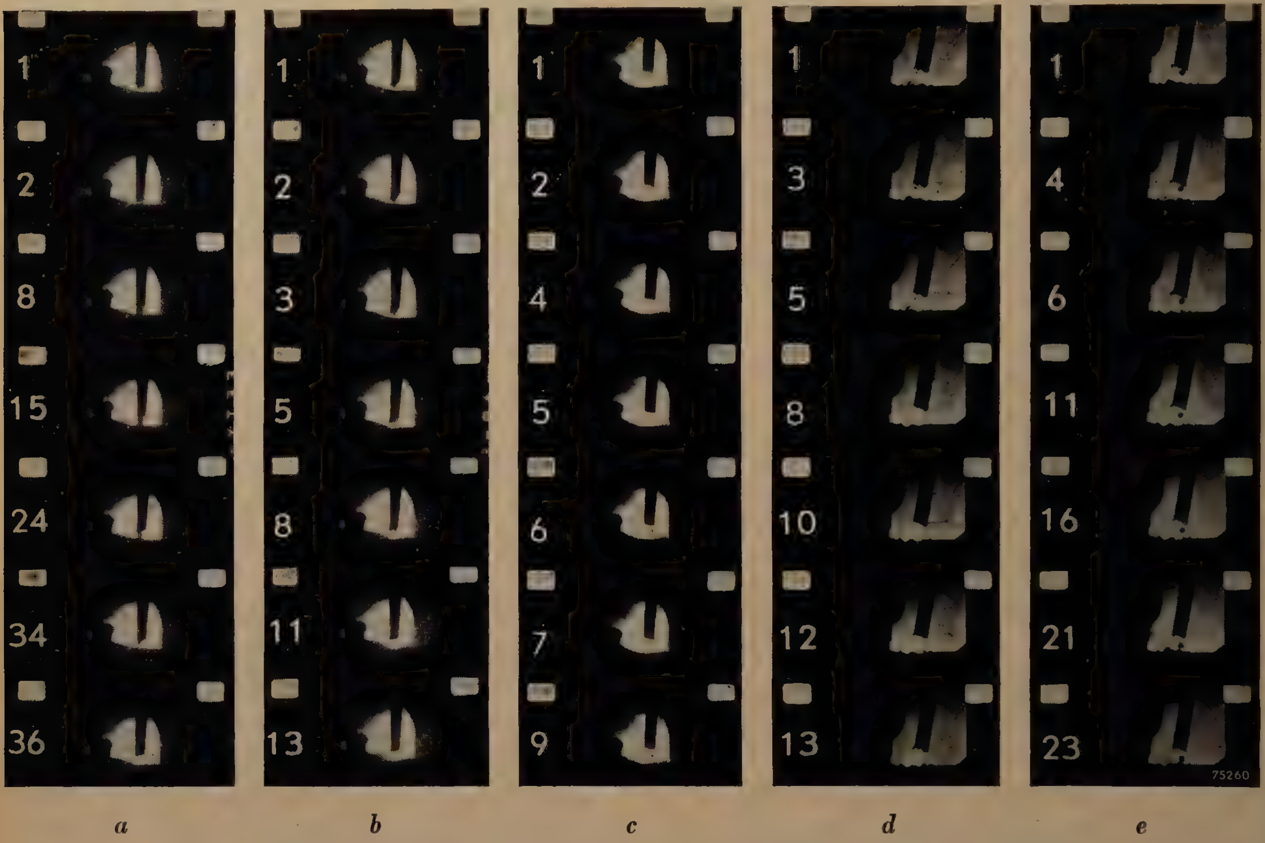

Fig. 6. Silhouette pictures of droplet transfer in arc welding. Some of the intermediate frames have been omitted from each strip, as will be seen from the numbering. These reproductions do not do justice to the film as exhibited; for example, it is barely possible to see from the above whether the arc is burning or not, whereas in the actual film the arc can be clearly seen to extinguish and re-ignite.

a) Metal transfer from Philips 48-5 gas-shielded electrode. The short-circuiting of the arc is clearly visible, starting at the moment the alternating current passes through zero and lasting almost one whole cycle ($^1/_{50}$ sec.). Film speed 2000 frames/sec.

b) Further pictures of the Philips 48-5 electrode. In frames 1, 2 and 3 the arc is extinguished (current=zero). In 2 there is a momentary short circuit, but no material is transferred. From 5, 8, 11 and 13 it will be seen that the arc exerts a force on the droplet, thus distorting it (see H. von Conrady, Der Werkstoffübergang im Schweisslichtbogen, Elektroschweissung 11, 109-114, 1943.)

c) With the contact electrode C18-4, which is derived from Philips 48 electrode, the metal transfer is in the form of small droplets. Weld made with free arc.

d) The low-hydrogen (basic) electrode, Philips 56-5. Two free droplets are seen, the upper one of which has the dimensions of the characteristic droplet ($d_c/D = 0.57$). The arc is extinguished only in frame 3.

e) The Philips 56-5 again. Here a large droplet is seen in process of being transferred. The arc is extinguished in 1 and 23. The 23 frames represent one half-cycle of the A.C. (1/100 sec).

The "optical efficiency"

In order to gain some impression whether the transfer of weld metal was actually recorded quantitatively on the film, the volume of material (iron and slag) transferred per second was first determined from the measured droplet diameters. This result was then divided by the volume of iron and slag per second ascertained from the actual weight of the quantities of material deposited and the known specific gravities. For the C18-4 this "optical efficiency" was found to be 100%, which of course it should be. The basic electrodes gave values of 150 to 200%, and the Philips 50 only

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[11]) J. Sack, Overhead welding, Philips tech. Rev. 4, 9, 1939.

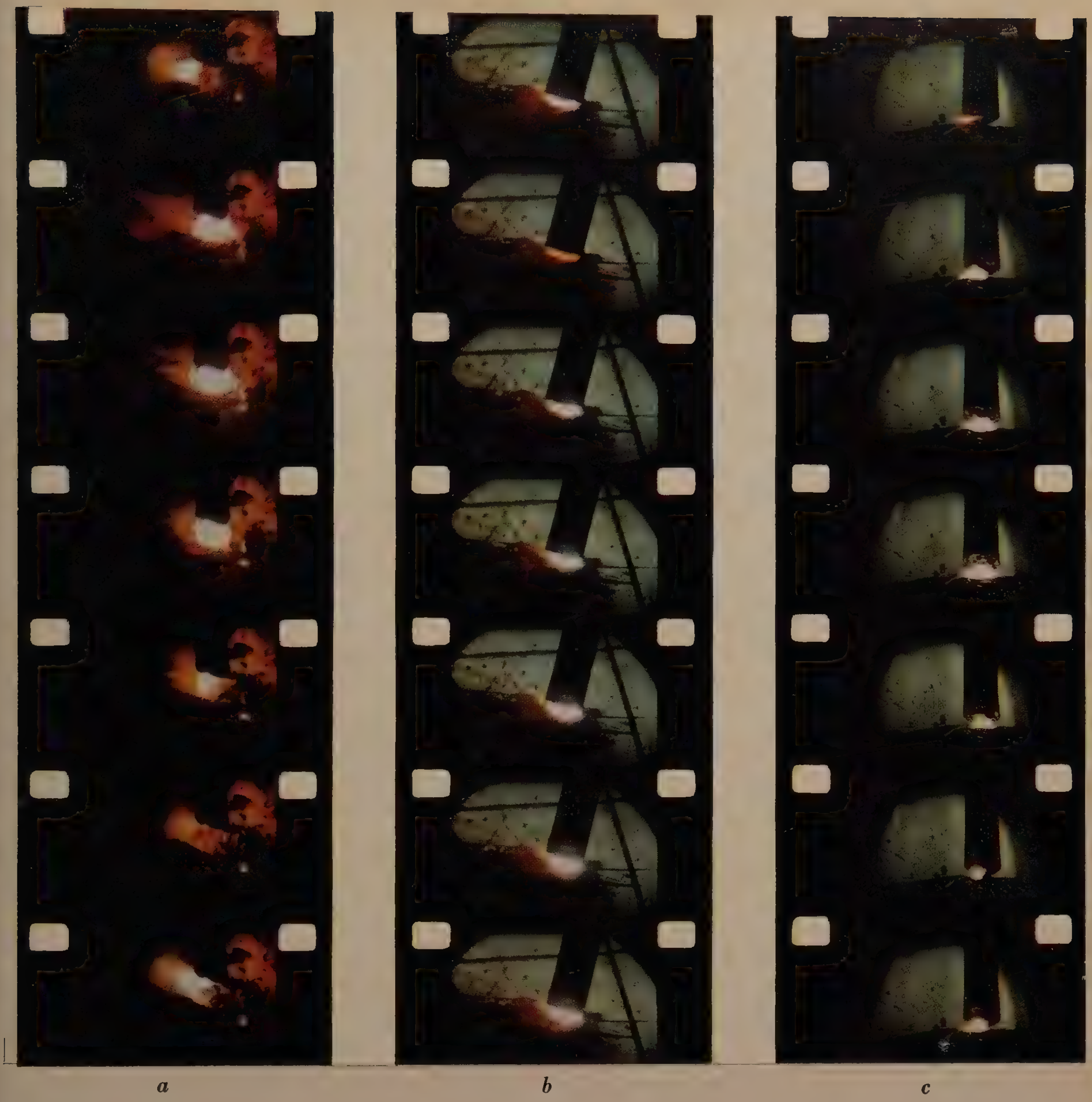

Fig. 7. Extracts (not sequential) from three colour films of arc welding with A.C. The differences in colour between the films are due to the use of different filters. (*a*) and (*b*) were filmed with the set-up shown in fig. 8; (*c*) with that of fig. 9.

a) Philips 50-5. In the top and bottom frames the arc is just re-igniting after the current has passed through zero. The air-blast used for dispersing the smoke also tends to blow away the arc. In the last frame but one the arc is extinguished (current passes though zero). Note the spatter on the right-hand side.

b) Contact electrode C20-4 developed from the Philips 50. The electrode is now touching the work. The arc is almost entirely shrouded by the cup formed by the coating and therefore burns quietly. No spattering is seen, and the arc is not affected by the air-blast used for dispersing the smoke. The arc is able to withstand a much greater air velocity than Philips 50 before it begins to "stutter". The current passes through zero in the second frame from the top.

c) Contact electrode drawn across the work at an angle that affords a view into the cup. The arc is extinguished in the top picture and is almost out in the last but one. It is clearly seen that the arc originates in the core of the electrode and that, irrespective of the direction of the current, it fans out towards the work.

50%. By moulding the droplets from the basic electrodes in a synthetic resin and then cutting them through, it was shown that many of these droplets contained cavities. Hence the droplet volumes observed from the film were greater than their true volumes. (In normal welding, the droplets merge in the liquid pool and the cavities entirely disappear.)

In the case of the Philips 50 electrode, a number of droplets were apparently not observed; these were presumably quantities of very small droplets which had been rendered invisible by the smoke, or by the fact that their silhouettes were indistinguishable from blemishes in the film. Clearly, in this case, the value of d_c obtained for this electrode, which is already very low, is nevertheless too high.

Colour films

In addition to the black and white silhouette films, some films were also made which were intended to give an overall picture of the welding process. On the advice of Prof. J. Brillié of Paris, these films were taken in colour (*fig. 7*). The light source was mounted so as to illuminate the work at slightly more than grazing incidence (*figs. 8* and *9*). The camera was similarly mounted, so as to photograph the work from an angle. In order to get as much reflected light as possible into the camera, the surface of the work was polished before each shot; in spite of this, so much light was lost that the arc was much brighter than the background.

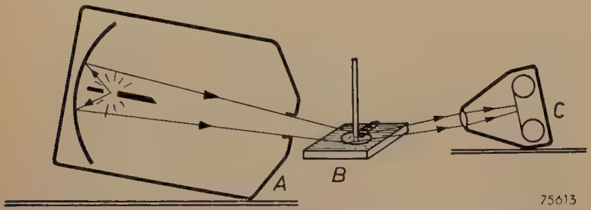

Fig. 8. Path of the rays in filming with reflected light using carbon arc lamp A as light source. This is the set-up used for taking the colour films. B welding arc. C camera.

The advantage of filming from an angle is that the pool of metal under the arc, with the layer of liquid slag on its surface, is then clearly visible. This gives a good perspective view of the welding processes. In addition to the advantage of more or less natural colouring, the use of colour film — owing to its laminated structure — gives pictures almost entirely free from the halation that otherwise occurs when the camera is directed towards the light source. With black and white films, halation is found to be a drawback at the beginning of the shot, when the camera has not yet attained its proper speed and the exposure time is accordingly too long.

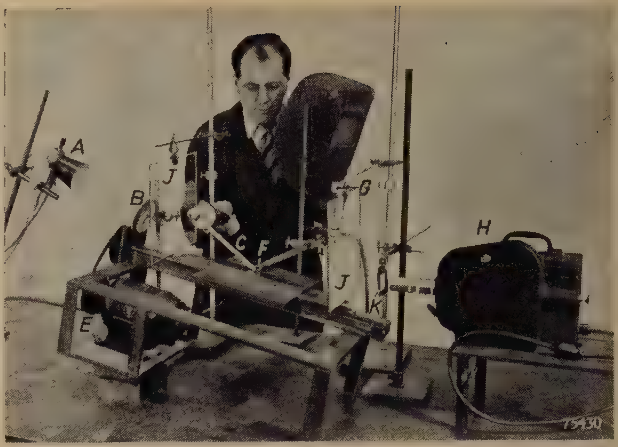

Fig. 9. Apparatus used for filming the processes in the crater of a contact electrode. The strip shown in fig. 9c was filmed in this manner. For meanings of letters A to J see fig. 4. K filter (Scott GG 3). The welding electrode has again been whitened. The weld is made in the plane defined by the light source A (here, a high pressure mercury arc) and the optical axis of the camera (instead of as in fig. 8, where the weld is shown along a direction perpendicular to this plane).

The series of pictures reproduced in fig. 7 are taken from three of these colour films. One series shows welding with an electrode with free arc (a), and the other two show contact welding with contact electrodes.

These films demonstrate the steadier arc and smaller spatter losses when the contact electrode is used; they also show the shape of the arc. The filming with the contact electrode at an oblique angle, giving a view into the cup (see figs 9 and 7c), confirms that the end of the core metal is always covered with a layer of slag during welding.

Summary. Systematic measurements have been carried out to ascertain the size of the droplets of weld metal transferred from welding electrodes to the work. For this purpose, films of the welding arc were made at a picture frequency o fup to 3000 per second. For the background a light of such brightness was used that the droplets were filmed in silhouette, notwithstanding the brilliant light emitted by the arc itself. Some of the measurements are discussed.

Colour films have also been made, at the same frequency, to give a more general impression of the processes taking place during welding. Certain features observed in the film are briefly reviewed.

BOOK REVIEWS

Fluorescent lighting: A review of the scientific and technical fundamentals and of the applications of the fluorescent lamp and its accessories. Editor-in-chief Prof. Dr. C. Zwikker, pp. 262, 187 illustrations. — Philips Technical Library — This book can be ordered through your technical bookseller.

The rapid evolution of the fluorescent lamp may be compared with that of the metal filament lamp (1907) and that of the gasfilled lamp (1913). On each of these occasions a new light source was introduced, of higher efficiency than its predecessor and of a colour making it suitable for general use.

The new tubular fluorescent lamp has been adopted so rapidly that nowadays practically all important new lighting installations for shops, restaurants, offices and factories use these lamps. The introduction of this new light source, however, has not been so simple as the changeover from the early incandescent lamp to its successor. The tubular shape demanded completely new fixtures. Control gear had to be built-in, and preferably in such a way that it would be unobtrusive. The usual method of increasing the lighting, namely by substituting a bigger lamp for a smaller one cannot be applied with fluorescent lamps, so that such lighting project has to be very accurately planned. In short, the development of the new lamp was not the end of the story. A new approach was also necessary with regard to fittings and to lighting schemes.

Anybody applying fluorescent lamps without taking into account these considerations, should be prepared for disappointing results.

For these reasons the publication of this book is highly appreciated. Under supervision of Prof. Dr. C. Zwikker, nine authors, all of the technical or scientific staff of Philips, have discussed the various aspects of fluorescent lighting. A summary of the subjects as given below.

Dr. J. L. Ouweltjes:	Luminescence, fluorescence and phosphorescence, and luminescent substances.
Dr. A. A. Kruithof:	Colour of the light emitted by tubular fluorescent lamps; colour rendering.
Dr. W. Elenbaas :	Gaseous discharges, lamp construction, and factors affecting the efficiency.
Drs. J. Funke :	Lamp types, starter switches, circuits.
Th. Hehenkamp :	Ballasts.
Ir. L. M. C. Touw :	Lighting fittings for fluorescent lamps.
Dr. D. Vermeulen :	Some fundamentals of lighting technique.
Ir. L. C. Kalff :	Applications of "TL" lamps.
Dr. R. v.d. Veen :	Uses of fluorescent lamps for agricultural purposes.

The book is amply and well illustrated; the picture of the colour triangle (fig. 19) and the energy-conversion graph on page 83 should be specially mentioned.

An extensive index of subjects renders valuable service to those interested only in certain parts of the subject.

The book is a very successful example of teamwork. There is a perfect balance as regards the various chapters, and overlappings and recurrences have been avoided. The book gives concise theoretical expositions as well as practical hints. It can be used not only by electrical engineers, but also by technicians, and by architects and physicists who wish to get acquainted with the present state of fluorescent lighting.

The reviewer's appreciation of this book can be best expressed by the remark that it is a great pity that a similar book has never been published on the gas-filled lamp.

N. A. HALBERTSMA.

Gas Discharge lamps, by P. J. Oranje, with a preface by M. Maurice Leblanc (President of the French Committee on Lighting and Heating and Vice-President of the International Lighting Committee), pp. 290, 161 figures and 32 photographs. — Philips Technical Library — This book can be ordered through your technical bookseller.

This is the English translation of the Dutch book by P. J. Oranje on discharge lamps. Since the publication of the Dutch edition, it has been brought up to date and supplemented by new material so as to correspond with the present state of the technique.

The book covers not only discharge lamps but also auxiliary gear, ballasts, fixtures and applications. As far as the last subject is concerned, the book contains some beautiful pictures of lighting installations. The lamps discussed are: sodium vapour lamps, mercury vapour lamps (high-pressure and ultra-high pressure lamps with forced cooling by air or water), neon lamps, stroboscopic lamps and finally fluorescent lamps.

With the aid of numerous diagrams and characteristics the author discusses the fundamentals of discharge lamps and also matters concerning the auxiliary gear and installations. The construction of the lamps and the auxiliary gear is also explained with diagrams and pictures. The mutual influence of the lamp and its auxiliary gear is dealt with in detail. An interesting appendix gives dimensions and characteristics of the Philips products in this field.

As head of the discharge lamp testing department of Philips for many years, Mr. Oranje was enabled to become well acquainted with the problems of lamp construction and installation. The text represents the experience gained in that way, supplemented and arranged in order in a critical manner. This book has been written by a man who is not content with summarising previous publications, but who has gone through all the facts he describes and who has been obliged to *solve* many of the problems arising in this field.

The book gives an answer to numerous questions relating to the use of gas discharge lamps, and will greatly contribute to the elimination of wrong ideas, which are still only too prevalent.

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ABSTRACTS OF RECENT SCIENTIFIC PUBLICATIONS OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN

Reprints of these papers not marked with an asterisk * can be obtained free of charge upon application to the address on the back cover.

2024: A. A. Kruithof: Specification of light sources by the spectral band method (C.I.E. Proceedings, Stockholm 1951, Vol. 3).

The specification of light sources by the spectral band method, as introduced by Bouma, is examined. For 10 pigments, illuminated by standard illuminants A or C, the displacement r of the colour point in the colour diagram, caused by a 10 percent increase in energy in a band 5 mμ wide about the wavelength λ, is calculated as a function of λ. The ratio r/r_A (where r_A is the radius vector of the corresponding McAdam ellipse) is plotted against λ. The area under the envelope of these curves is divided into 7 or 8 parts thus obtaining the following bands:

380-445-485-525-560-595-625-750 mμ
and 380-445-470-500-530-560-595-625-750 mμ.

By a separate investigation it is shown that for a band between 380 mμ and x mμ, the displacement of the colour λ point by concentrating the luminance of the band into one wavelength (436.8 mμ) is a minimum for $x = 445$ mμ. The distributions found satisfy the condition that the mercury lines 546 mμ and 578 mμ shall not be too near the limit of a band.

2025: B. Verkerk: A possible extension of the density-difference method of spectrographic analysis (J. Opt. Soc. America **41**, 1017-1022, 1951).

An investigation into the use of Seidel's "transformed density" $D_t = \log [(d_0/d)-1]$, in which d_0 and d are the densitometer deflections of the unexposed plate and the spectral line, respectively. An empirical formula is derived for D_t as a function of the illumination E. Using this formula it is possible to estimate the error introduced if the D_t-log E curve is considered as a straight line for interpolation according to the density-difference method. This proves permissible under certain specified conditions in the density range 0.1—2. The influence of the wavelength on the shape of the transformed density curve is investigated and some experimental results obtained with the method are described.

2026*: G. W. Rathenau: Etude des phénomènes de récristallisation par microscopie électronique à émission (Revue Métallurgie **48**, 923-928, 1951, No. 12). (Study of recrystallisation by emission electron-microscopy; in French).

Description of a method for studying crystal growth by means of emission electron-microscopy. Results with face-centered NiFe alloys show, after intensive rolling, a cubic structure with (001) planes parallel to the rolling plane and the [100] direction parallel to the rolling direction. It is proved that, in general, crystal limits with highest energy are displaced, but it is impossible to predict whether crystals having a large surface energy will grow or dissappear. The former occurs in normal crystal growth, starting from small grains, the latter in secondary recrystallization. Most probably after primary recrystallization, large crystals are in the most favourable condition for growing. (See No. **1986**.)

2027: G. D. Rieck and J. M. Stevels: The influence of some metal ions on the devitrification of glasses (J. Soc. Glass Tech. **35**, 284-288, 1951, No. 167).

A study, at 1200 °C, by means of X-ray spectrometer diagrams, of the crystallization of glasses containing about 95 mole % SiO_2 and about 5 mole % of Li_2O, Na_2O, K_2O, BeO, MgO, CaO, BaO or ZnO. The univalent ions are shown to promote the formation of tridymite from initially formed cristobalite. The glasses with bivalent ions devitrify by formation of cristobalite. A number of these ions influence the crystallization in such a way that it starts with the temporary formation of quartz. Probably this is due to a direct influence of these ions on the glass, and not to an indirect influence on the transformation of the crystalline phases.

2028: W. Six: Het gebruik van koude-kathodebuizen als schakelelement (T. Ned. Radiogenootsch. **17**, 17-32, 1952, No. 1). (Cold cathode gas discharge tubes as switching element; in Dutch).

This paper points out that there is an electronic analogy for most circuits which can be built up with electromechanical parts, such as relays, switches, etc. A small cold-cathode gas-filled valve has been developed to be used as switching-element in electronic circuits.

Examples are given of equivalent electronic circuits for relays circuits, counting-and selecting-circuits, registers, busy-test and lock-out circuits and for talking-path circuits.

2029: M. Travniçek, F. A. Kröger, Th. P. J. Botden and P. Zalm: The luminescence of basic magnesium arsenate activated by manganese (Physica **18**, 33-42, 1952, No. 1).

In the system $MgO\text{-}As_2O_5$ there is a compound of the composition $6MgO.As_2O_5$. Products containing small concentrations of manganese show fluorescence upon excitation by cathode rays or by ultra-violet radiation. The band emitted depends on the valency of the mangenese. Divalent manganese causes fluorescence in a broad band in the green, with a maximum at 5050 Å. Tetravalent manganese causes a red fluorescence in five narrow bands at 6200 Å, 6300 Å, 6500 Å and 6580 Å. Both fluorescences decay exponentially; the time constant at room temperature is 130 sec^{-1} for the green band and 360 sec^{-1} for the red bands. For the red luminescent systems the spectral distributions of the absorption, excitation and fluorescence and the temperature dependence of the intensity of the fluorescence, the fluorescence spectrum and the decay constant have been determined, and a quantitative explanation of several of these values has been given.

2030: J. A. Haringx: De wondertol (De Ingenieur **64**, O13-O17, 1952, No. 4). (The magic top (Tippe Top); in Dutch).

Starting from the analysis of a series of forced regular precessions the author has shown why and under what conditions the "tippe top" exhibits its typical behaviour. The limits of the ratio of its principal moments of inertia with respect to the eccentricity of its centre of gravity have been determined and the minimum initial rotation which is needed for reversal has been calculated.

2031: J. M. Stevels: Les pertes diélectriques des verres et les renseignements qu'elles donnent pour l'étude de leur structure (Silicates industrielles **16**, 325-328, 1951, No. 10; **17**, 15-18, 1952, No. 1). (Dielectric loss in glasses and its relevance to the study of their structure; in French).

The power factor ($\tan \delta$) of glasses is discussed as a function of the frequency (f), the temperature (T) and the chemical composition, both from a theoretical and a practical point of view. A three-dimensional model, showing the relation between $\tan \delta, f$ and T is described. The influence of chemical composition on the power factor is discussed at some length.

R185: J. L. H. Jonker, A. J. W. M. van Overbeek and P. H. de Beurs: A decade counter valve for high counting rates (Philips Res. Rep. **7**, 81-111, 1952, No. 2).

A decade counter tube has been developed having a ribbon shaped electron beam and 1-dimensional deflection. The electrode configuration resembles that of a cathode-ray tube and is such that the beam can be fixed in any of ten discrete positions. Slotted electrodes permit part of the beam to fall on the appropriate part of a fluorescent layer, so that the instantaneous position can be read from the adjacent figure on the wall of the tube. The beam moves from one position to the next when an impulse is applied to one of the deflection electrodes. Counting and calculating devices constructed with these tubes permit a great economy in valves and components, in comparison to conventional counting circuits, The decade counter tube has small dimensions (the size of a normal receiving valve), low power consumption and low supply voltage (300 V). For random pulses the tube has a mean resolving time of about 15 µsec when connected in a simple counting circuit. With the aid of one double triode this can be improved to 6 µsec. With a special circuit incorporating a triode-hexode and a secondary-emission tube it has been reduced to less than 0.2 µsec. For pulses occurring at equal intervals the resolving time is larger. See also Philips tech. Rev. **14**, 313-326, 1953 (No. 11).

R186: J. A. Haringx: Instability of thin-walled cylinders subjected to internal pressure (Philips Res. Rep. 7, 112-118, 1952, No. 2),

See Abstract No. **1997**.

R187: P. Schagen, H. Bruining and J. C. Francken: A simple electrostatic electron-optical system with only one voltage (Philips Res. Rep. 7, 119-130, 1952, No. 2).

A simple electron-optical system is described for application in television pick-up tubes or image converters. This system consists of two concentric spheres, the sphere with the smaller radius, the anode, being provided with a hole. The electron paths in the field of force of this system are calculated and the influence of the hole in the anode is estimated. The calculations indicate that an inverted image of the cathode can be obtained at a distance equal to $6(n-1)R_a/(n-4)$ behind the hole, the magnification of this image being equal to $3/(n-4)$, where n is the ratio of the radii of the spheres and R_a represents the radius of the anode sphere. With experimental tubes, adapted to practical requirements, pictures of good resolution and geometry have been obtained.

R188: A. E. Pannenborg: On the scattering matrix of symmetrical waveguide junctions (Philips Res. Rep. 7, 131-157, 1952, No. 2).

The description of the electromagnetic behaviour of microwave circuits with the aid of the scattering matrix is systematically developed. Special attention is paid to resonators. The basic results obtained by Tomonaga on this subject are elaborated to the point of practical usefulness.

R189: J. M. Stevels: Some experiments and theories on the power factor of glasses as a function of their composition, III (Philips Res. Rep. 7, 161-168, 1952, No. 3).

It is shown that the power factor of borosilicate glasses (measured for widely differing frequencies) is a minimum on the straight line separating the accumulation region and the destruction region in the phase diagram, thus showing that on this line the rigidity of the network is a maximum. This maximum is less pronounced for the higher SiO_2 concentrations and vanishes at composition of 75% SiO_2-20.5% B_2O_3-4.5% M_2O (M = Na or Li). The experimental results are discussed from a theoretical point of view.

See abstracts **R 127** and **R 158.**

R190: A. E. Pannenborg: On the scattering matrix of symmetrical waveguide junctions, II (Philips Res. Rep. 7, 169-188, 1952, No. 3).

Continuation of **R 188**. General considerations about the consequences of structural symmetry of microwave circuits lead up to an extensive dicussion of junctions consisting of two parallel sections of rectangular waveguide.having one of their sides in common.

R191: J. A. Haringx: Instability of bellows subjected to internal pressure (Philips Res. Rep. 7, 189-196, 1952, No. 3).

See No. **1998.**

R192: Th. P. J. Botden: Transfer and transport of energy by resonance processes in luminescent solids, II (Philips Res. Rep. 7, 197-235, 1952, No. 3).

Continuation of **R178.** A number of sensitized systems are dealt with. Of the several explanations for the phenomenon of sensitization, only a few are borne out by experiment. On the basis of some of these theories it has been deduced that the ratio of the quantum efficiencies of activator and sensitizer fluorescence will not increase with increasing sensitizer concentrations at constant activator concentration. This is found to be in contradiction with the author's results, obtained with the systems $Ca_3(PO_4)_2$-Ce-Mn, $Sr_3(PO_4)_2$-Sn-Mn, $Ca_5P_3O_{12}F$-Sb-Mn, $Ca_2P_2O_7$-Sn-Mn and also with Fröhlich's results on $Mg_2P_2O_7$-Ce-Th-Mn. An explanation of the experiments is given on the basis of: (1) a random distribution of the sensitizer and the activator ions, (2) direct transfer of energy from the sensitizer to a neighbouring activator (by quantum-mechanical resonance), (3) the assumption that if the excited sensitizer has not an activator in its neighbourhood, the excitation energy may be transferred via other sensitizer ions (by resonance) to a sensitizer that *has* an activator in its neighbourhood, followed by transfer of the energy to the activator. The numbers of cation sites around a sensitizer are calculated from the experiments on a few systems, for transfer both to an activator and to another sensitizer. The mechanisms of transfer and transport of energy are discussed on the basis of the theory of Mott and Seitz; the temperature dependance of sensitization may be explained in this way.